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Contents

Electrofiltration: A New Method of Removing Exchangeable Bases from Soil-Colloids. AMAR NATH PURI..... 413

Relation of Ash Constituents of Pasture Plants to the Oxidation-Reduction Potentials of Nutrients. H. P. COOPER AND J. K. WILSON..... 421

Influence of Inorganic Nitrogen Compounds on Reaction and Replaceable Bases of Norfolk Sand. R. M. BARNETTE AND J. B. HESTER..... 431

Nitrogen and Organic Matter in Hawaiian Pineapple Soils. A. L. DEAN. 439

The Oxidation of Pyrite and Sulfur as Influenced by Lime and Magnesia—A 12-Year Lysimeter Study. W. H. MACINTIRE, W. M. SHAW, AND J. B. YOUNG..... 443

The Laws of Soil Colloidal Behavior: III. Isoelectric Precipitates. SANTE MATTSON..... 459

Index..... 497

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ELECTROFILTRATION: A NEW METHOD OF REMOVING EXCHANGEABLE BASES FROM SOIL COLLOIDS

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Received for publication April 8, 1930

The method of separating crystalloids from colloids by diffusion, accelerated by an electric current, is well known in colloid chemistry. The literature on the subject has been summed up by Humfeld and Alben (2). The application of this principle to soil problems is chiefly due to Mattson, whose work on electrodialyzed clays is well known. He has shown, for instance, that exchangeable bases in soils can be determined by this method, and the results obtained agree with those obtained by neutral salt displacement.

The Mattson cell consists of three compartments separated by a semipermeable membrane, such as parchment. The colloidal solution is placed in the middle section, and the outside ones are filled with distilled water. One of the outside sections contains a platinum gauze anode, and the other a copper or nickel cathode. When a potential difference of 20 to 200 volts is applied at these electrodes, the exchangeable bases collect as hydroxides in the cathode compartment, and can be determined by simple titration.

Bradfield, who confirmed Mattson's results (1), introduced a two-compartment cell consisting of an alundum extraction thimble, which is supported by a nickel cathode suspended in a specially constructed glass cell with a side arm. The platinum foil anode is placed on the inside of the alundum thimble. By a constant-level arrangement that maintains a flow of water, the exchangeable bases that appear in the cathode are continuously removed. The electrodialysis is continued until the dialysate gives no coloration with phenophthalein.

While working on similar lines, it appeared to the author that the technique could be further simplified to make possible the employment of the method for routine work in soil laboratories. With that object in view, two apparatuses, A and B, were devised and are described in the following. As will be seen later, they are based on a slightly different principle from the one hitherto employed, and for the sake of convenience of reference the name "Electrofiltration" is proposed.

APPARATUS A

Apparatus A is shown in figure 1. It consists of a glass cylinder (about 2.5 inches in diameter), a perforated copper disc provided with a screw for electrical connections, and a glass funnel provided with a flange, fitting exactly against

the flange of the cylinder. Attached to the perforated disc are two copper rings with diameter slightly greater than the flanges of the funnel and the cylinder, and in which the latter fit snugly. A filter paper (preferably Watman 50) is placed on the copper disc and the flange of the cylinder is dipped

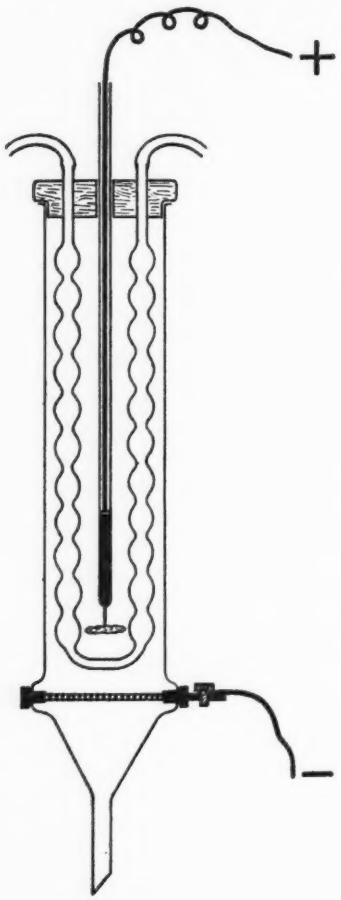

FIG. 1. DIAGRAM OF ELECTROFILTRATION APPARATUS A

into molten wax; after the excess wax is shaken off, the cylinder is attached to the disc with the filter paper interposed between. The flange of the funnel is also dipped into molten wax and attached to the other side of the disc. The flanges of the cylinder and funnel are then clamped together by brass rings provided with thumb screws (not shown in the diagram). Later it was found

preferable to have rubber washers attached to the flanges of the cylinder and the funnel.

The cathode is the copper disc, and the anode a platinum wire gauze. Attached to the wooden lid holding the anode is a U-tube for circulating cold water when the apparatus is running. The electrodes are connected to the electric main, and the current density is kept below 0.5 ampere by a lamp resistance. The current flowing through the apparatus is further regulated by moving the anode up or down as required. The apparatus can be left running overnight because when the level of water goes down below the anode the current is automatically shut off. Ten to twenty grams of the soil can be used at a time and the filtration is fairly rapid, for the tendency of the soil colloids is to move upward toward the anode, therefore there is no risk of the filter paper being clogged.

When the level of the water goes down, more is poured in, therefore a constant-level device was not found necessary. In fact the apparatus can be left to take care of itself after being started, and water filled in again when the first lot has more or less filtered through. The filtrate is collected all together or in several lots and titrated for total bases. It is better to back-titrate after adding excess of standard acid, as suggested by Bradfield. When the filtrate gives no color with phenolphthalein all the exchangeable bases have been removed. The anode is lifted along with the cooling device when the experiment is over. The apparatus can be dismantled, hot water being used for dislodging the wax, and can be reassembled in about 10 minutes.

It might be noted that there is no limit to the size of the apparatus. From a specimen jar 6 inches in diameter and with the base knocked off, the top of a vacuum desiccator, and a perforated brass disc having raised rims, an electrofiltration apparatus was assembled, with the help of rubber washers and suitable clamps, which worked quite satisfactorily, and could deal with about 500 gm. of soil at a time. Two U-tubes were used for cooling in this case.

APPARATUS B

Apparatus B, shown diagrammatically in figure 2, is much simpler, and very suitable for preparing soils free from exchangeable bases. It consists of a glass funnel and a perforated copper cone, which serves as the cathode. The anode is a platinum gauze (a platinum wire shaped into a coil serves equally well) attached to a glass tube, held in a wooden cover which also holds a V-shaped glass tube (not shown in the diagram) for circulating water. A filter paper is fitted into the copper cone as in ordinary filtration, and after the cone is filled with soil suspension the electrodes are connected with the electric main as in apparatus A.

Instead of a stout perforated cone, a nickel or copper gauze shaped like a cone can be used. A stout filter paper is preferable, but almost any brand can be used. The amount of soil that can be treated at a time depends on the size

of the apparatus, for which there is no limit. Sometimes the filtration is too rapid, and a stop-cock attached to the funnel is required to regulate the flow.

A battery of half a dozen electrofilters can be conveniently run, thus effecting a great saving of time for routine work.

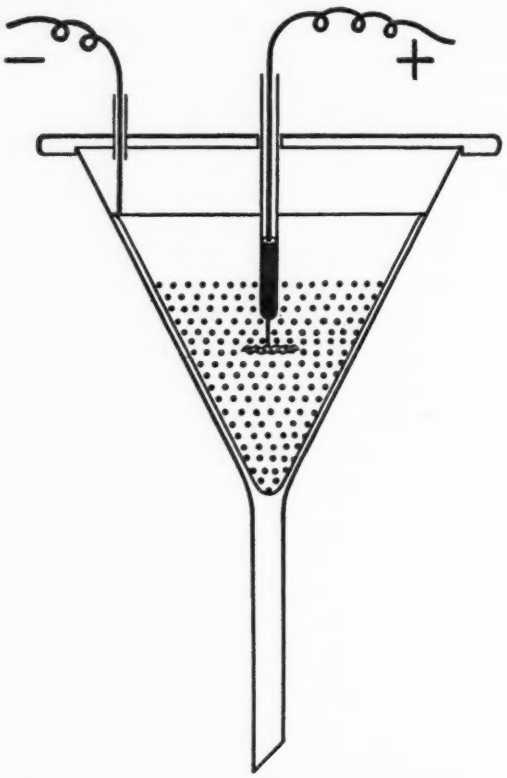

FIG. 2. DIAGRAM OF ELECTROFILTRATION APPARATUS B

ESTIMATION OF EXCHANGEABLE BASES IN SOILS

A very useful application of the electrofiltration method lies in the estimation of exchangeable bases in soils. It must be recognized, however, that only in the case of soils free from calcium carbonate, will the method give results identical to those obtained by neutral salt reaction. It is necessary that in the application of such methods we should differentiate between exchangeable bases and free bases present as carbonates. The removal of the latter by the neutral salt reaction methods, is purely a solubility effect, whereas in electro-

filtration or electrodialysis the reaction is electrochemical, and a greater amount of the carbonates is removed from the soil.

In table 1 are given the total bases removed in successive hours by electrofiltration (apparatus A), from a number of soils. The current was about 0.2 ampere and the weight of the soil 10 gm. in every case.

It will be seen from table 1 that the time required for the removal of bases by electrofiltration depends on the nature of the soil: soils 1 and 2 are calcarious and soil 6 is highly acid. The method as it stands, makes no distinction between exchangeable bases, and free bases present as carbonates. With this limitation, the electrofiltration method can be considered a rapid means of characterizing soils, and should afford some useful information regarding soil reaction.

TABLE 1

Bases removed by electrofiltration in successive hours from various soils

TIME	BASES (MILLIEQUIVALENTS) REMOVED					
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5	Soil 6
hours						
1	4.01	3.90	3.21	0.86	1.40	0.13
2	1.98	2.37	0.74	0.47	0.88	0.08
3	1.46	2.35	0.41	0.18	0.60	0.04
4	1.34	0.65	0.27	0.06	0.05	0.01
5	1.16	0.17	0.15	0.04	0	....
6	1.10	0.34	0.10	....	....	....
7	1.09	0.20	0.09	....	....	....
8	0.57	0.09	0.07	....	....	....
9	0.56	....	0.08	....	....	....
10	0.42	....	....	....	....	....
11	0.28	....	....	....	....	....

ELECTROFILTRATION AS A MEANS OF DISPERSING SOILS FOR MECHANICAL ANALYSIS

Both Mattson and Bradfield have drawn attention to the easy dispersibility of electrodialyzed soil when treated with sodium hydroxide. A similar conclusion was reached by the author from his studies with soils treated with dilute hydrochloric acid; and it appeared of interest to compare the electrofiltration method with other preliminary treatment of the soil for mechanical analysis. Forty soils from different parts of India were used for comparison with three methods: the electrofiltration method, the (NaCl-NaOH) method developed by the author (3), and the 0.05 *N* HCl method of Puri and Amin (4).

In the electrofiltration method, the soil is electrofiltered for five or six hours, and then transferred with a jet of water to a stout beaker. Then 0.1 *N* NaOH is gradually added till the suspension is alkaline to phenolphthalein, tested by

TABLE 2

Mechanical analysis of soils by different preliminary treatments

SOIL NUMBER (P.C.)	MECHANICAL ANALYSIS				
	Silt (0.02 mm.)		Clay (0.002 mm.)		
	Electrofiltration method	(NaCl-NaOH) method	Electrofiltration method	(NaCl-NaOH) method	0.05 *N* HCl method
	per cent	*per cent*	*per cent*	*per cent*	*per cent*
8	3.5	7.0	27.2	25.2	23.9
9	15.7	14.8	22.7	21.6	14.6
10	11.0	14.5	36.5	35.6	35.6
11	11.6	11.1	31.4	32.8	30.6
12	16.1	20.5	6.0	3.8	7.2
13	20.4	19.6	56.4	58.9	56.7
14	23.7	23.8	16.0	22.3	21.5
15	21.4	26.2	20.5	21.9	22.0
16	15.1	16.5	9.6	7.3	8.7
17	23.4	23.5	14.7	14.2	14.1
18	62.8	61.4	20.6	22.2	22.6
19	17.4	19.6	41.5	42.4	40.7
20	9.4	9.2	8.1	6.5	8.1
21	26.1	28.9	16.3	13.5	14.6
22	17.2	16.3	14.5	15.2	13.9
23	13.1	13.8	10.8	11.3	11.1
24	14.4	21.2	14.0	8.0	9.7
25	4.1	2.2	3.7	4.0	3.7
26	5.3	4.2	23.3	22.6	23.5
27	21.1	16.3	42.3	53.2	51.1
28	15.9	21.3	48.7	44.6	43.0
29	18.4	21.3	58.1	63.0	61.2
30	18.6	21.1	52.4	54.1	52.0
31	7.1	10.2	24.7	22.8	22.6
32	24.4	20.8	62.5	62.9	64.6
34	41.5	42.9	13.1	11.3	12.5
35	19.4	20.9	18.9	18.3	19.8
36	13.1	11.9	12.3	11.7	12.0
37	21.8	21.1	9.2	4.1	5.9
38	18.9	20.0	51.4	52.9	51.2
39	10.5	9.5	10.4	8.5	8.9
40	6.7	6.5	12.6	13.1	13.0
41	17.0	22.8	50.6	53.4	51.4
42	19.1	22.9	50.6	53.4	52.8
43	38.1	36.5	11.6	19.7	21.6
44	20.3	19.2	8.8	8.4	9.1
45	17.9	18.0	11.8	10.7	11.1
46	17.6	16.6	55.2	56.4	54.0
47	29.4	32.7	16.7	17.1	16.4
48	27.3	30.8	19.8	19.8	19.6

taking a drop on a tile or by throwing a drop of the indicator on the suspension. No shaking is necessary but the suspension is occasionally stirred during the course of six hours.

In the 0.05 *N* HCl method the soil was washed with 0.05 *N* HCl till the filtrate was free from Ca ions, 0.1 *N* NaOH then being added exactly as above.

In the (NaCl-NaOH) method, the soil was washed with *N* NaCl followed by leaching with only a small quantity of water. Sodium hydroxide was then added to make the suspension alkaline to phenolphthalein, as stated in the foregoing.

The results given in table 2 show that all three methods give closely agreeing values for clay, and the choice of any one of them may be a matter of personal inclination.

The mechanical analyses were done by the pipette method, the technique described by Puri and Amin (4) being used. All values refer to air-dry soils.

SUMMARY

Two forms of electrofiltration apparatus for removing exchangeable bases from soil colloids have been described.

Electrofiltration can be used as a preliminary treatment of the soil for mechanical analysis, and gives closely agreeing values for clay with the (NaCl-NaOH) method and the 0.05 *N* HCl method, which have already been shown to effect complete dispersion of soil colloids.

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RELATION OF ASH CONSTITUENTS OF PASTURE PLANTS TO THE OXIDATION-REDUCTION POTENTIALS OF NUTRIENTS

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The lack of a close correlation between the hydrogen-ion concentration of soils and the growth of plants leads to a consideration of the electrical potential relations which may result from the presence in the soil of ions above and below hydrogen in the electromotive series. Since many organisms are known to absorb selectively, metallic nutrient ions in the same qualitative order as they appear in the electromotive series, it appeared desirable to determine the ash constituents of plants representing the pasture plant associations characteristic of the various soil fertility levels found in New York pastures. These associations and their ecological significance are described in previous papers (6, 8). A more or less characteristic succession of pasture plants accompanies the depletion of such soils. The particular species which dominates at the various fertility levels is often determined by climatic conditions. Kentucky bluegrass which requires a fertile soil may be followed by redtop in relatively dry climates or by Rhode Island bent grass in cooler climates with relatively high growing-season rainfall.

Kentucky bluegrass requires a fertile soil, and it is likely to dominate on the productive soils. As the soil is depleted, Rhode Island bent grass or redtop encroaches upon the Kentucky bluegrass and may finally dominate. On further depletion of the soil sweet vernal grass may dominate, and finally poverty grass, weeds, and trees represent the dominant type of vegetation (8).

SELECTION OF MATERIAL FOR ANALYSIS

The samples were taken when the grasses were in full bloom or shortly thereafter. The samples of Kentucky blue and sweet vernal grasses were collected during June and early July. The Rhode Island bent and poverty grasses were obtained three or four weeks later, since they do not bloom as early as do the Kentucky blue and sweet vernal grasses. When the samples of grass were taken the soils on which they were growing were sampled and their hydrogen-ion concentrations determined potentiometrically.

Most of the Kentucky bluegrass samples were taken from Ontario loam, which is a limestone soil. Many of the other samples were taken from non-limestone soils. The Rhode Island bent, sweet vernal, and poverty grass samples were collected from the Wooster, Volusia, and Gloucester series. The broomsedge sample was from Merrimac sandy loam.

TABLE 1

Analyses of pasture grasses representing the various plant associations characteristic of the different soil fertility levels found in New York pastures

NUMBER OF SAMPLE	pH OF		PER CENT OF DRY MATTER						
	Soil	Subsoil	K_2O	CaO	MgO	P_2O_5	SiO_2	N	Ash
Kentucky bluegrass—Poa pratensis									
1	7.84	7.63	2.77	0.14	0.18	0.54	3.87	1.56	7.52
2	6.99	6.83	2.42	0.16	0.18	0.57	1.63	1.53	6.12
3	6.91	....	1.65	0.27	0.18	0.47	1.05	1.14	4.68
4	6.70	....	1.79	0.31	0.21	0.47	0.77	1.48	4.61
5	7.79	....	1.79	0.24	0.18	0.42	1.11	1.21	4.41
6	6.85	6.80	3.02	0.11	0.22	0.71	3.77	1.79	8.23
7	6.64	6.83	2.84	0.14	0.16	0.74	1.69	1.91	6.79
8	5.51	5.64	2.62	0.18	0.19	0.76	1.38	1.79	6.26
9	5.92	5.97	2.33	0.08	0.13	0.49	1.89	1.19	5.70
Average...	6.79	6.62	2.36	0.18	0.18	0.57	1.91	1.51	6.04
Per cent of ash.....			39.07	2.98	2.98	9.44	31.62	25.00	
Bent grasses—Agrostis tenuis and Agrostis canina									
1	5.19	5.31	2.08	0.34	0.16	0.39	1.10	1.49	5.18
2	4.48	4.67	2.16	0.19	0.14	0.64	2.17	1.40	6.30
3	5.75	5.76	1.45	0.38	0.21	0.34	3.03	1.47	6.11
4	5.18	5.25	0.78	0.43	0.32	0.32	2.76	1.35	5.09
5	5.15	5.15	2.34	0.41	0.21	0.47	1.81	1.46	5.90
6	5.30	4.81	1.68	0.38	0.19	0.34	2.59	1.16	5.77
7	4.80	4.69	1.90	0.36	0.23	0.39	1.44	1.26	4.95
8	4.90	....	1.61	0.36	0.19	0.39	2.01	1.17	5.27
9	4.87	4.30	1.50	0.33	0.16	0.34	2.99	1.26	5.73
10	4.30	5.40	1.75	0.44	0.16	0.39	2.79	1.42	6.28
11	7.51	7.51	0.85	0.23	0.11	0.39	4.10	1.64	6.29
12	5.08	5.23	0.39	0.25	0.21	0.32	3.57	1.07	5.23
13	5.02	5.40	0.48	0.21	0.13	0.32	2.88	0.99	4.43
Average...	5.19	5.29	1.46	0.33	0.19	0.39	2.56	1.32	5.58
Per cent of ash.....			26.16	5.91	3.40	6.99	45.88	23.65	
Sweet vernal—Anthoranthum odoratum									
1	5.38	5.42	1.74	0.19	0.13	0.35	1.06	1.13	4.23
2	5.22	5.76	1.88	0.22	0.13	0.32	1.00	1.13	4.33
3	5.22	5.34	2.14	0.11	0.13	0.52	1.31	1.23	5.02
4	5.92	5.97	2.04	0.12	0.13	0.44	1.25	1.10	4.89
5	5.35	5.48	1.56	0.18	0.13	0.40	1.02	0.95	3.92
6	4.61	4.67	1.70	0.14	0.11	0.42	1.25	1.13	4.21
Average...	5.28	5.44	1.84	0.16	0.13	0.41	1.15	1.11	4.43
Per cent of ash.....			41.53	3.61	2.93	9.25	25.96	25.06	

TABLE 1—*Concluded*

NUMBER OF SAMPLE	pH OF		PER CENT OF DRY MATTER						
	Soil	Subsoil	K_2O	CaO	MgO	P_2O_5	SiO_2	N	Ash
Poverty grass—Danthonia spicata									
1	4.61	5.31	1.24	0.27	0.13	0.17	1.77	0.67	3.99
2	6.87	5.68	1.43	0.27	0.11	0.17	0.68	0.64	3.27
3	5.97	5.80	1.37	0.28	0.13	0.22	1.13	0.99	3.44
4	4.95	5.05	1.74	0.25	0.14	0.28	1.44	1.02	4.29
5	5.55	5.48	1.47	0.26	0.16	0.26	0.78	1.10	3.47
Average...	5.59	5.46	1.45	0.27	0.13	0.22	1.16	0.88	3.69
Per cent of ash.....			39.29	7.32	3.52	5.96	31.44	23.85	
Broomsedge—Andropogon virginicus									
1	4.74	5.04	0.40	0.19	0.05	0.30	4.21	0.71	5.14
Per cent of ash.....			7.78	3.70	0.97	5.84	81.91	13.81	

ASH CONSTITUENTS OF THE GRASSES COLLECTED

The chemical composition of certain of the grasses which were collected are shown in table 1. The figures represent the composition of those plants which compose the most common plant successions accompanying the depletion of soils in New York pastures.

The nitrogen and the silica-free ash contents of these plants seem to decrease as the soils become depleted. Potassium, reported as the oxide, constitutes from about one-third to two-fifths of the ash content of common pasture plants. It is relatively high in Kentucky blue and sweet vernal grasses, whereas it is relatively low in Rhode Island bent and poverty grasses. The Rhode Island bent and poverty grasses contain the largest quantities of calcium. This inverse relationship between the content of potassium and calcium in the different grasses seems to be related to the grand growth period of the species. Plants, such as Kentucky blue and sweet vernal grasses, with their grand growth period early in the season are relatively high in potassium and low in calcium, whereas the species with their grand growth period coming relatively late in the season are higher in calcium and lower in potassium.

A negative correlation of -0.87 ± 0.023 was found between the K_2O and CaO content in the ash of 45 samples of pasture plants (6). An average of 0.18 per cent of CaO was found in the ash of Kentucky blue and 0.33 per cent in the ash of Rhode Island bent grass. This is an interesting relationship, since the Kentucky bluegrass samples were taken from limestone soil. The average pH value of 6.79 given in table 1 indicates that the soils were well supplied with available calcium. Most of the Rhode Island bent samples were taken from non-limestone soils. The average pH value of the soils on

which the Rhode Island bent grass was found is 5.19. The inverse relationship between the quantities of potassium and calcium in the plants analyzed would seem to indicate that the ash constituents of plants are largely determined by the amounts of these constituents which are available in the soil. These data are in agreement with the growth response of Kentucky bluegrass to potassium fertilization, as reported by White and Holben (26) and by White and Gardner (27).

TABLE 2

Analyses of grasses found in some New York pastures

NUMBER OF SAMPLE	pH OF		PER CENT OF DRY MATTER						
	Soil	Subsoil	K_2O	CaO	MgO	P_2O_5	SiO_2	N	Ash
Canadian bluegrass—Poa compressa									
1	7.80	....	1.58	0.21	0.11	0.34	0.46	1.05	3.56
2	7.63	7.63	1.08	0.33	0.13	0.17	3.07	0.68	5.14
3	7.57	....	1.06	0.23	0.16	0.17	0.80	0.79	2.64
4	7.57	....	0.99	0.34	0.18	0.22	1.02	0.78	3.10
Average...	7.64	7.63	1.18	0.28	0.15	0.23	1.34	0.83	3.61
Per cent of ash.....			32.69	7.76	4.15	6.37	37.12	22.99	
Orchard grass—Dactylis glomerata									
1	7.58	....	2.90	0.19	0.16	0.71	1.66	1.23	6.84
2	7.47	7.35	4.71	0.11	0.20	0.87	2.65	2.10	10.16
Per cent of ash.....			44.70	1.76	2.12	9.41	25.29	19.53	
Rice cut grass—Leersia oryzoides									
1	5.09	....	0.49	0.19	0.13	0.36	9.29	0.97	10.93
2	5.26	....	0.53	0.23	0.21	0.50	7.02	1.40	9.07
Average...	5.17	....	0.51	0.21	0.17	0.43	8.15	1.18	10.00
Per cent of ash.....			5.10	2.10	1.70	4.30	81.50	11.80	

The average quantities of phosphorous, reported as P_2O_5, in the ash of Kentucky bluegrass and sweet vernal grass is relatively high; on the other hand, the phosphorus content of the Rhode Island bent and poverty grasses is relatively low. This appears to be a significant relationship. The phosphorous content is positively correlated with potassium and negatively correlated with calcium in 45 samples (6). A positive correlation of $+0.76 \pm 0.043$ was observed between K_2O and P_2O_5 in the ash of plants, and a negative correlation of -0.44 ± 0.08 between the CaO and P_2O_5. It is probable that under certain conditions both plants and animals can assimilate the phosphorous of potassium phosphates more readily than that of calcium phosphates.

The potassium phosphates are more soluble than calcium phosphates, and they have a much higher ionization coefficient, which probably facilitates the reduction of the phosphate ion to a phosphite ion. The ease with which phosphorus is assimilated is probably dependent upon the reduction of the phosphate ion either by radiant energy, as from the sun, or by the free energy decrease in oxidation-reduction reactions (6).

There is a negative correlation between the P_2O_5 and SiO_2 in the ash of the plants studied (6). The sample of broomsedge was found to be very high in silicon.

Certain of the ash constituents of Canadian blue, orchard, and rice cut grasses are shown in table 2. Both the total ash and the nitrogen content of the Canadian bluegrass samples are low. This species probably tolerates a lower fertility level than does Kentucky bluegrass. The rice cut grass is very high in silicon. It is probable that silicic acid or other silicates is playing a rôle in the nutrition of both rice cut grass and broomsedge.

A summary of the analytical data is given in table 3. It is observed that the nitrogen and the silica-free ash tend to decrease as the soils are depleted. The nitrogen ranges from 1.51 per cent in Kentucky bluegrass to 0.71 per cent in broomsedge. The average contents of K_2O, CaO and MgO in the plants are 1.33 per cent, 0.22 per cent and 0.14 per cent respectively, which is in agreement with the order of these elements in the potential series. These data demonstrate the correlation between the order of electropositive elements in the electromotive series and their relative amounts in the ash of plants.

REMOVAL OF ASH CONSTITUENTS OF PLANTS FROM SOIL COLLOIDAL COMPLEXES AND ABSORPTION OF NUTRIENT IONS

Since materials with relatively high standard electrode potentials, such as potassium or calcium, are often the predominant metallic constituents of plants, it is interesting to note the qualitative order of removal of cations from soil colloidal complexes by electrodialysis. Koenig, et al. (15) noted that some of the potassium is easily removed from the soil. Their results from the electrodialysis of six soils show that the amount of potassium removed was more than five times that of the magnesium. Recent data reported by Mattson (16, 17, 18) and Wilson (28) may be interpreted to show that there is a correlation between the qualitative order of removal of metallic exchangeable atomic cations from soil colloidal complexes by electrodialysis and their arrangement in the electromotive series. The work of Gedroiz (13) on base exchange shows a similar relationship.

The order of removal of atomic cations from soil colloidal complexes is also probably closely correlated with the ionization potentials of elements. The approximate energy of removal, in equivalent volts, of the inmost normal valence electron of elements to form ions is as follows: Cs^+ 3.87 volts, Rb^+ 4.15 volts, K^+ 4.30 volts, Na^+ 5.13 volts, Li^+ 5.40 volts, Ba^{++} 9.96 volts, Sr^{++} 10.98 volts, Ca^{++} 11.82 volts, H^+ 13.54 volts, Mg^{++} 14.97 volts, and

Al^{+++} 28.32 volts (9, 12, 22). There is probably a closer agreement between the order of removal of atomic cations from exchange complexes of soil by electrodialysis and the preceding grouping than there is with the electromotive series or displacement grouping of elements.

The foregoing values suggest an interpretation for the relatively large amounts of hydrogen ions in certain soil colloidal complexes. Hydrogen comes between calcium and magnesium in the foregoing grouping. There is usually a relatively small amount of exchangeable magnesium in the colloidal complex of most non-saline soils. Such elements as aluminum with an energy

TABLE 3

Nutrient elements in the ash of pasture grasses representing the various plant associations characteristic of the different soil fertility levels found in New York

GRASS	NUMBER OF SAMPLES	AVERAGE pH	K_2O	CaO	MgO	P_2O_5	SiO_2	N	ASH
Average per cent of dry weight									
Kentucky blue	9	6.79	2.36	0.18	0.18	0.57	1.91	1.51	6.04
Rhode Island bent	12	5.19	1.46	0.33	0.19	0.39	2.56	1.32	5.58
Sweet vernal	6	5.28	1.84	0.16	0.13	0.41	1.15	1.11	4.43
Poverty	5	5.59	1.45	0.27	0.13	0.22	1.16	0.88	3.69
Broomsedge	1	4.74	0.40	0.19	0.05	0.30	4.21	0.71	5.14
Rice cut	2	5.17	0.51	0.21	0.17	0.43	8.15	1.18	10.00
Average			1.33	0.22	0.14	0.39	3.19	1.12	5.81
Average per cent of the ash of plants									
Kentucky blue	9	6.79	39.07	2.98	2.98	9.44	31.62	25.00	
Rhode Island bent	12	5.19	26.16	5.91	3.40	6.99	45.88	23.65	
Sweet vernal	6	5.28	41.53	3.61	2.93	9.25	25.96	25.06	
Poverty	5	5.59	39.29	7.32	3.52	5.96	31.44	23.85	
Broomsedge	1	4.74	7.78	3.70	0.97	5.84	81.91	13.81	
Rice cut	2	5.17	5.10	2.10	1.70	4.30	81.50	11.80	
Average			26.49	4.27	2.58	6.96	49.72	20.53	

of removal of the inmost normal valence electron of 28.32 equivalent volts would be expected to form complex ions in most non-saline soils.

Data on ash analysis of 48 plants reported by Robinson, et al. (23) show the order of mineral constituents as follows: K_2O 34.36 per cent, CaO 19.63 per cent, MgO 7.13 per cent, Al_2O_3 1.34 per cent, and Fe_2O_3 0.61 per cent. Aston (2, 3, 4) reports data on the constituents of 70 samples of pasture plants, which include samples from regions of New Zealand where iron is deficient in forage plants. His average data for 47 to 70 samples are as follows: CaO 1.05 per cent, MgO 0.47 per cent, Al_2O_3 0.13 per cent, Mn_3O_4 0.045 per cent, and Fe_2O_3 0.041 per cent. These data are in general agreement with the analyses

reported in this paper. All of these data show that many plants selectively absorb the strong ions or the elements with relatively high standard electrode potentials.

RELATION OF SOIL FERTILITY AND LIGHT REQUIREMENTS OF PLANTS TO THEIR FOOD VALUE

A book by Orr (22) contains an excellent summary of data on the mineral content of pasture plants, therefore only recent data of particular interest are cited in this paper. The relation to nutrition of electrochemical factors which are of interest in this connection have been discussed in previous papers (6, 7, 8). The differential absorption of the stronger ions may limit or exclude essential but weaker nutrient materials such as magnesium, manganese, and and iron. Jones (14) found that a deficiency of available magnesium in the soil was responsible for chlorosis of certain crops. Magnesium is apparently the most electropositive element in the chlorophyll complex.

The common chemical fertilizers usually contain materials which form strong ions, therefore an application of fertilizer may very materially affect the chemical composition of plants. The affect of nitrogenous fertilizer in increasing the nitrogen content of the plant has been reported by Enlow and Coleman (11). Data reported by Archibald and Nelson (1) and by Ellenberger, et al. (10) show that applications of chemical fertilizer increased the yield and modified the composition of pasture plants. Brown and Slate (5) have reported on the growth response of pasture plants to the various fertilizer constituents.

The available data on both growth response and chemical analysis indicate that nutrient materials which form strong ions are usually the factors limiting the production of pastures in humid climates (6, 7, 8). The fertility of the soil greatly affects the quality as well as the total production of pastures. A discussion of the rôle of pastures in the mineral nutrition of farm animals by Maynard (20) is of interest in this connection.

The available data suggest that plants which require fertile soils and strong ions for their optimum growth also require light of high quality. Many plants which grow normally on poor soil and endure weak nutrient ions are often tolerant of shade and are of low food value.

The absorption of radiant energy of quality equal to or greater than the free energy decrease in the formation of simple electrolytes from elements greatly facilitates their assimilation (6). In the case of electrolytes composed of compound ions, like phosphates, with low ionization coefficients, the absorption of energy equivalent to the decomposition or discharge potentials greatly facilitates their assimilation. Maughan (19) found that radiation of 2,968 Ångstrom units or 4.16 equivalent volts is near the center of the most important radiation involved in the cure of rickets. This value is very near the decomposition or discharge potential of calcium phosphate, which is 4.20 equivalent volts. This shows that calcium phosphate is light stable to near

the short wave limit of the solar spectrum, which is around 4.26 equivalent volts (6). Either plants or animals using calcium phosphate will require light of high quality for its optimum assimilation. Ammonium and hydrogen phosphates, which have lower discharge potentials than calcium phosphate, probably do not require as short waves of light for their assimilation. Therefore, plants which endure acid soil and relatively weak nutrient ions are often very tolerant of shade. As previously noted, phosphorous in the form of potassium phosphate is usually relatively easily assimilated because it has a high ionization coefficient, which probably facilitates the reduction of the phosphate ion to a phosphite ion. This reduction is probably necessary for the optimum assimilation of phosphorous. Since there is a positive correlation between the K_2O and P_2O_5 in the ash of pasture grasses and a negative correlation between the CaO and P_2O_5 in the ash content of pasture grasses, this suggests that potassium is often a very important element in the growth of early season plants such as Kentucky bluegrass. Available potassium can be increased by a direct application of potassium or indirectly by treating the soil with other material which may affect the availability of potassium in the soil.

Vitamins A and D present in cod liver oil probably have their origin in sea plants. Sea water might be considered as a rich nutrient medium, and as plants selectively absorb strong ions sea plants would probably require relatively short waves of light for their optimum development. The absorption of large quanta of energy would probably result in the synthesis of organic compounds which on oxidation would be capable of supplying large quanta of energy (6). Since life is a reduced system, the oxidation of organic materials will result in a free energy decrease and the emission of radiant energy. The size of the quanta emitted will probably be influenced by the energy level at which the various organic compounds are synthesized.

Von Euler, et al. (25) have identified vitamin A with lipochrome pigments. Positive results were obtained in growth experiments with carefully purified carotin from carrots as the sole source of vitamin A. They conclude that the effect of vitamin A in the blood is due to its oxidation-reduction action. Experiments with carotin by Moore (21) have confirmed some of the conclusions of Von Euler, et al.

Certain data (6) definitely suggest that many vital processes are on an energy level in close agreement with the free energy decrease in the formation of certain simple electrolytes, and with the reduction potentials of some common nutrient ions such as nitrates, borates, sulfates carbonates, and phosphates.

SUMMARY AND CONCLUSIONS

Data are reported on certain ash constituents of the grasses representing the most common plant successions accompanying the depletion of soils in New York pastures.

The nitrogen and the silica-free ash contents of the grasses seem to decrease as the soils become depleted.

Elements with relatively high standard electrode potentials, such as potassium and calcium, are often the predominant mineral constituents in the ash of plants.

A strong negative correlation was observed between the potassium and the calcium content of the ash of pasture grasses.

It is suggested that there is a correlation between the qualitative order of removal of atomic metallic cations from soil colloidal complexes by electrodialysis and the order of the energy of removal, in equivalent volts, of the inmost normal valence electron of elements.

Many organisms differentially absorb atomic nutrient cations in the same qualitative order as they are removed from soil colloidal complexes by electrodialysis.

Plants which require fertile soils or strong nutrient ions for optimum growth are often intolerant of shade and require large quanta of radiant energy for optimum growth. Plants which normally require a rich nutrient medium and large quanta of radiant energy may synthesize organic compounds which, on oxidation, would be capable of supplying large quanta of radiant energy and may be of high food value, whereas plants which grow normally on poor soils and endure weak nutrient ions are often shade tolerant and of relatively low food value.

The absorption of radiant energy of quality equivalent to or greater than the free energy decrease in the formation of simple electrolytes from the elements may greatly facilitate their assimilation by organisms.

There is a wide difference in the quality of radiant energy necessary for the reduction of the common nutrient anions. Phosphorous is one of the most difficult to reduce, ultraviolet light being required for its reduction. Phosphorous in compounds with relatively high ionization constants is often relatively easily assimilated, since phosphorous in ionic form is probably more easily reduced than is phosphorous in molecular form.

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INFLUENCE OF INORGANIC NITROGEN COMPOUNDS ON REACTION AND REPLACEABLE BASES OF NORFOLK SAND

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A number of grass plats have been established[2] at the Florida Agricultural Experiment Station at Gainesville for the purpose of studying the growth habits and the fertilizer requirements of lawn and golf green grasses in Florida. The plats are established for the most part on the typical deep phase of the Norfolk sand of this section. Clay lies from 8 to 10 feet below the substrata of yellow and surface soil of gray sand.

A series of these plats is devoted to lawn grasses, chief among which are Saint Augustine grass (*Stenotaphrum secundatum* Walt. Ktze.) and centipede grass (*Eremochloa ophiuroides* Munro. Hack). These plats were established in April, 1923, and are continued to date. One-third of each plat of grass is fertilized with sodium nitrate at the rate of 1,333 pounds an acre yearly applied in 12 monthly top-dressings. One-third receives ammonium sulfate at the rate of 1,000 pounds an acre yearly applied at the same time as the sodium nitrate and equivalent in nitrogen content to it. One-third remains unfertilized. During 1926 and 1927 four of these plats were selected for a study the effect of sodium nitrate and ammonium sulfate on the pH values of aqueous suspensions of the soil. Samples were made from the third of each of the four plats receiving the different nitrogenous fertilizer salts.

The determination of the H-ion concentration was made on the fresh samples, one part of the soil being used to approximately three parts of distillled water. The suspensions were allowed to stand overnight and the pH value of the clear supernatent liquid was determined by the indicator method with the double-wedge standards. The results were checked by two indicators when the range permitted.

The average results of 11 determinations on composite samples removed from the 0–6-inch depth of the soil from the variously fertilized areas of the plats during 1926 and 1927 are given in table 1.

It is noted that the individual parts of the plats receiving the same source of

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nitrogen vary very little within themselves. The results indicate that the sodium nitrate has increased the alkalinity of the soil and the ammonium sulfate has increased the acidity. The effect has not been great in either the acid or alkaline direction but the differences are significant because of the large number of determinations averaged, and the consistency of the results.

A series of plats devoted to the study of putting green grasses was sodded to various strains of Bermuda grass (*Capriola dactylon* L. Kuntze) in the spring of

TABLE 1

Average pH values of aqueous soil suspensions made on composite soil samples during 1926 and 1927*

TREATMENT	PLAT 1	PLAT 2	PLAT 3	PLAT 6	AVERAGE
	pH	*pH*	*pH*	*pH*	*pH*
No fertilizer	6.91	6.88	6.87	6.99	6.91
Sodium nitrate	6.98	7.00	6.98	7.02	7.00
Ammonium sulfate	6.63	6.72	6.82	6.70	6.71

* Average of 11 determinations at different times.

TABLE 2

Average pH values of aqueous soil suspensions made on composite soil samples during 1926 and 1927*

TREATMENT	PLAT 1	PLAT 2	PLAT 3	PLAT 4	PLAT 6	AVERAGE
	pH	*pH*	*pH*	*pH*	*pH*	*pH*
Norfolk sand						
No fertilizer	6.54	6.55	6.59	6.61	6.61	6.58
Ammonium sulfate	6.26	6.27	6.19	6.24	6.41	6.15
Ammonium phosphate	6.40	6.31	6.35	6.41	6.44	6.38
Norfolk sand top-dressed with 2–3 inches of clay						
No fertilizer	6.00	6.23	6.40	6.43	6.34	6.25
Ammonium sulfate	5.72	6.18	6.14	6.33	6.22	6.05
Ammonium phosphate	6.03	6.22	6.25	6.33	6.25	6.19

* Average of 11 determinations at different times.

1925. One half of each 10 by 25-foot plat received a top-dressing of approximately three inches of clay, the other half remaining the deep sandy soil. Across both the sand and clay parts of the plats, one-third of each plat is fertilized with ammonium sulfate and one-third receives ammonium phosphate (Ammo-phos, 20–20), whereas the middle third has no fertilizer treatment. The ammonium sulfate and ammonium phosphate are applied at the rate of 1,000 pounds an acre yearly in fractional semi-monthly top-dressings. Five of these plats were selected for a study of the influence of ammonium sulfate

and ammonium phosphate on the pH values of aqueous suspensions of the soil. Samples were taken from both the clay top-dressed and sandy ends of the plats to a depth of approximately six inches. Eleven determinations of the pH values of the aqueous suspensions were made during 1926 and 1927 by the method described. The averaged figures obtained on the various plats are given in table 2.

The ammonium sulfate has lowered the pH value of an aqueous suspension of the soil more than has the ammonium phosphate. The change has been greater in the sand than in the clay top-dressed halves of the plats. These results are in accord with the data of Pierre (2) who found that ammonium sulfate increased the H-ion concentration of aqueous soil suspensions more than did ammonium phosphate and that the change in H-ion concentration induced by a given nitrogenous source was dependent upon the buffer capacity of the soil.

TABLE 3

Effect of increasing amounts of ammonium sulfate on the pH value

YEARLY ADDITIONS OF AMMONIUM SULFATE TO THE ACRE	ORIGINAL	3 MONTHS*	8 MONTHS†	10 MONTHS‡	21 MONTHS
pounds	*pH*	*pH*	*pH*	*pH*	*pH*
None	6.76	6.63	6.53	6.33	6.47
1,000	6.78	6.51	6.44	6.29	6.21
2,000	6.73	6.39	6.31	6.12	5.89
3,000	6.45	6.37	6.30	6.05	5.43
5,000	6.60	6.30	6.02	5.89	4.45

* Average of determinations made at end of second and third month after first application of ammonium sulfate.

† Average of determinations made at end of fourth, fifth and sixth month.

‡ Average of determinations made at end of ninth and tenth month.

A third series of plats was established to Bermuda grass in 1926 and increasing quantities of ammonium sulfate, applied every two weeks as a dressing, are used as a source of nitrogen on these plats. A series of samples representing a composite sample of the 0–12-inch depth of the soil of these plats was taken for about 21 months after the beginning of the experiment.

The pH values of the variously fertilized soils are given in table 3 for the different dates after the initiation of the experiment. In 21 months, the higher applications of ammonium sulphate have decreased the pH values of the aqueous soil suspensions from the original pH of approximately 6.6 to as low as pH 4.45, in the case of the 5000-pound application. This indicates the low buffer capacity of the deep phase of the Norfolk sand in Florida. The increase in H-ion concentrations has been proportional to the application of ammonium sulfate.

It is generally conceded that the removal of the bases of the soil by leaching

TABLE 4

Effect of increasing amounts of ammonium sulfate on replaceable bases and on the pH value of aqueous suspensions at different depths

Per 100 gm. of air-dried soil

ADDITIONS* OF AMMONIUM SULFATE	0–9 INCHES						9–21 INCHES						21–33 INCHES					
	Ca	Mg	Na	K	Total	pH	Ca	Mg	Na	K	Total	pH	Ca	Mg.	Na	K	Total	pH
pounds	*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*		*m.e.*	*m.e.*	*m.e.*	*m.e.*	*m.e.*	
None	2.464	0.800	0.194	0.149	3.607	6.57	1.964	0.500	0.129	0.085	2.678	6.66	1.821	0.400	0.194	0.149	2.564	6.28
1,000	1.929	0.650	0.226	0.128	2.933	6.16	1.786	0.600	0.161	0.149	2.696	6.26	1.750	0.350	0.129	0.106	2.335	6.05
2,000	1.179	0.550	0.194	0.149	2.072	6.01	1.321	0.500	0.194	0.085	2.100	6.18	1.286	0.400	0.097	0.085	1.868	5.84
3,000	0.928	0.400	0.161	0.085	1.574	5.76	1.393	0.350	0.065	0.085	1.893	5.93	1.557	0.400	0.097	0.064	1.918	5.76
5,000	0.786	0.400	0.065	0.106	1.357	5.59	1.179	0.300	0.065	0.064	1.608	5.76	1.250	0.350	0.097	0.064	1.761	5.76

* Additions on basis of pounds an acre yearly.

and by plants and the replacement of the cations Ca, Mg, Na, and K by the H ion is responsible for the development of an acid condition in the soil. In order to study the change in the replaceable base content of the deep phase of the Norfolk sand as induced by the different applications of ammonium sulfate, a series of samples at different depths was taken on August 4, 1927, or 17 months after the initial applications of ammonium sulfate and the establishment of the plats to Bermuda grass.

Six samples were taken from each plot to make a composite sample, each of which was thoroughly mixed and air-dried. Fifty grams of the samples were leached with one liter of *N* NH_4Cl to determine the replaceable cations. It was found necessary to use these proportions to obtain quantities of the bases which could be estimated with a fair degree of accuracy. For the determination of the Ca and Mg, 300 cc. of the ammonium chloride leachings were used, and 600 cc. were used for the estimation of the Na and K. The pH values were determined in a 1–2 soil-water suspension by the quinhydrone method.

TABLE 5

Effect of increasing amount of ammonium sulfate on relative total m.e. of replaceable bases

Untreated soil taken as basis

ADDITIONS OF* AMMONIUM SULFATE	0–9 INCHES	9–21 INCHES	21–33 INCHES
pounds			
None	100.0	100.0	100.0
1,000	81.3	100.6	91.0
2,000	57.5	78.5	72.8
3,000	43.6	70.6	74.8
5,000	37.6	60.0	68.6

* Additions on basis of pounds an acre yearly.

The replaceable cation content expressed as milligrams equivalent (m.e.) per 100 gm. of air-dried soil and the pH values of the aqueous soil suspensions are given in table 4. Increasing amounts of ammonium sulfate decrease the replaceable cation content of the soil. There is a correlation in the pH value of the aqueous suspension of the soil and the replaceable cation content for each depth of the soil. The higher the replaceable cation content of a given depth of soil the higher the pH value. The total capacity of the soil to combine with bases evidently decreases with depth, the higher content of the replaceable cations in the surface soil being associated with a higher organic matter content.

The replaceable cation content of the untreated soil being considered as 100, the percentages of the total replaceable cations found in the ammonium sulfate treated plats are calculated and given in table 5. From these calculations it can be seen that there is a decided decrease in the removal of the replaceable bases with an increase in the depth of the soil. There is also a corresponding

decrease in the effect of the ammonium sulfate in lowering the pH values of the lower depths of the soil. This is in accord with the results of Crowther (1) who found that there was a depth distribution of the effect of ammonium sulfate in decreasing the pH value of soils at Woburn and Rothamsted.

The divalent cations predominate in the soil complex. Calcium is presenting amounts far in excess of the other cations. In table 6 are given the relative proportions of the different cations in the replaceable state in the soil and the effect of the ammonium sulfate in changing these proportions in the various

TABLE 6

Distribution of Ca, Mg., Na, and K in every 100 m.e. of the replaceable cations in three depths of soil

ADDITIONS OF* AMMONIUM SULFATE	0–9 INCHES				9–21 INCHES				21–33 INCHES			
	Ca	Mg	Na	K	Ca	Mg	Na	K	Ca	Mg	Na	K
pounds												
None	68	22	5	4	73	19	5	3	71	16	8	6
1,000	66	22	8	4	66	22	6	6	75	15	6	5
2,000	57	27	8	7	63	24	9	4	69	21	5	5
3,000	59	25	10	5	74	19	3	5	71	21	5	3
5,000	58	30	5	8	73	19	4	4	71	20	6	4

* Additions on basis of pounds an acre yearly.

TABLE 7

Percentages of the total m.e. of cations lost by the ammonium sulfate treated plats at different depths accounted for by divalent and monovalent cations†

ADDITIONS OF* AMMONIUM SULFATE	0-9 INCHES		9-21 INCHES		21–33 INCHES	
	Ca + Mg	Na + K	Ca + Mg	Na + K	Ca + Mg	Na + K
pounds						
1,000	100.00	....	100.00	....	52.84	47.16
2,000	100.00	....	100.00	....	76.87	23.13
3,000	95.23	4.77	91.84	8.16	71.83	28.17
5,000	92.36	7.64	92.06	7.94	77.33	22.67

* Additions on basis of pounds an acre yearly.

† Calculations made on the basis of replaceable base content of the untreated plat.

depths. In these calculations the H ion and the Al ion have not been taken into consideration. As can be seen, the calcium is removed to a greater extent than the other cations.

With the cation content of the untreated soil as a basis, the losses in cations as distributed between the divalent and the monovalent ions have been calculated and the percentages of distribution are given in table 7. Although in all depths of the soil the divalent Ca and Mg make up the greater part of the loss, still in the 21–33-inch depth, particularly, the monovalent Na and K

account for a very much larger proportion of the loss, indicating a replacement of these cations by the Ca and Mg.

SUMMARY

A study was made of the influence of different carriers of nitrogen on the H-ion concentration of the deep phase of a Norfolk sand which was sodded to lawn and golf green grasses. The influence of increasing applications of ammonium sulfate on the replaceable cation content of the deep phase of the Norfolk sandy soil was also studied for the different depths of the soil. The results may be summarized as follows:

Ammonium sulfate increased the acidity and sodium nitrate the alkalinity of the deep phase of the Norfolk sand sodded to lawn grasses.

Ammonium sulfate increased the acidity of the deep phase of the Norfolk sand more than did ammonium phosphate which had been applied in amounts equivalent in nitrogen content.

A dressing of three inches of clay decreased the effect of both ammonium sulfate and ammonium phosphate in lowering the pH value of Norfolk sand (deep phase).

The decrease in H-ion concentration of the Norfolk sand (deep phase) induced by applications of ammonium sulfate was proportional to the amounts of ammonium sulfate applied, and correlated with a decrease in the total milligram equivalents cations in the replaceable state in the soil.

The effect of ammonium sulfate on the removal of replaceable cations and the effect on the H-ion concentrations of the soil decrease with depth of soil.

The divalent cations are predominate in the Norfolk sand (deep phase).

The application of ammonium sulfate decreases the replaceable divalent cation content to a greater extent than the replaceable monovalent cation content.

The losses of the replaceable cations in the Norfolk sand (deep phase) indicate a replacement of the monovalent cations in the lower depths of soil by the divalent cations.

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NITROGEN AND ORGANIC MATTER IN HAWAIIAN PINEAPPLE SOILS

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The following data are presented because of their possible bearing on the commonly accepted view that the carbon and nitrogen of soils tends toward a ratio of 10 to 1, and their failure to harmonize with the results reported by Jenny (1, 2) in his study of the influence of climate on soil nitrogen. Jenny does not attempt to extend the validity of his conclusions beyond the continental portions of the United States. His data are derived from the analyses of soils in central United States, chiefly in the regions between the Mississippi River and the Rocky Mountains, and support his conclusion that the nitrogen of the soil decreases with increase of the mean annual temperature.

The 223 soil samples, the nitrogen and organic content of which are here summarized, were taken from pineapple fields, or lands destined to become pineapple fields. They came from the islands of Hawaii, Maui, Lanai, Molokai, Oahu, and Kauai, from elevations ranging from 200 feet to 3,000 feet above sea level, and from locations where the rainfall ranges from less than 20 inches to approximately 100 inches yearly. The great majority of the samples were taken from the surface to a depth of 12 inches, a few to 18 or 20 inches, and in some cases, where the topsoil was thin, the sampling did not extend below 8 or 10 inches. Some of the soils were from uncultivated ranch lands, some had been in pineapples for 20 years or more. In short, they are an unselected group of soils, representing many thousands of acres of unirrigated lands, from localities where they have been exposed to different conditions. They have a similar origin in that they are all derived from basaltic lavas or cinders. The mean annual temperatures have not been precisely the same for all of them, but a representative figure would be 70°F. They would probably all fall within the range of 65° to 75°F. This is comparable to the warmest regions included in Jenny's series. The Hawaiian climate, however, is less variable than that of Texas and Lousiana and temperatures more than 15°F. on either side of the mean are unusual.

The organic matter has been determined[1] by the method of J. B. Rather (4).

[1] None of the analyses were made by me and they were not carried out for the purpose of investigating the subject here discussed. Prof. F. T. Dillingham of the University of Hawaii, and Messrs. F. A. E. Abel, Carl A. Farden, and L. A. Dean have done the analytical work.

The procedure was as follows:

Reagents: Acid—washed and ignited asbestos, 2.5 per cent hydrochloric acid, 2.5 per cent hydrofluoric acid.

Procedure: Weight out, by difference, 1-gm. samples of oven-dry soil [prepared as in the Official Methods of the Association of Official Agricultural Chemists edition of Sept. 1920, page 309, 2 (a)] into platinum dishes. Measure into a glass cylinder 30 cc. distilled water, 10 cc. 2.5 per cent HCl, and 10 cc. 2.5 per cent HF; mix, and pour the mixture carefully upon the soil sample. Place the whole upon a boiling water bath and digest it for exactly five minutes.

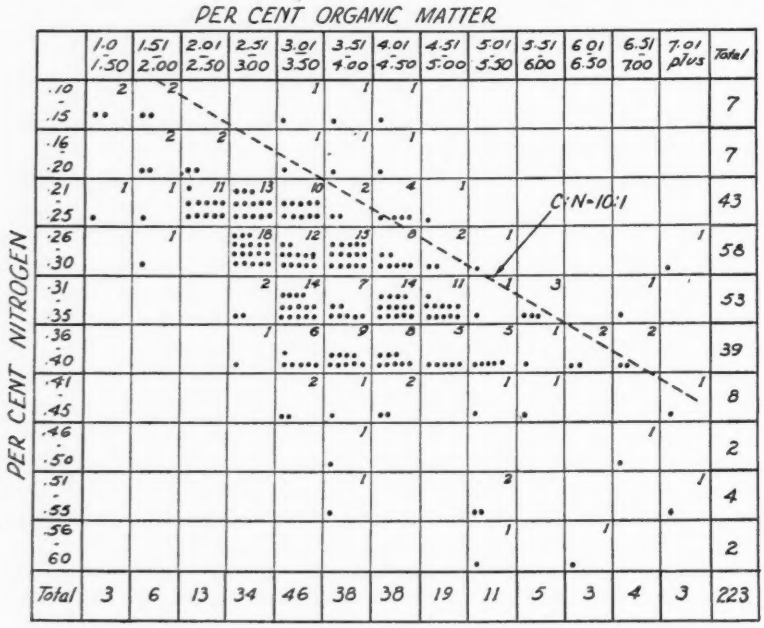

FIG. 1. DISTRIBUTION OF NITROGEN AND ORGANIC MATTER IN 223 HAWAIIAN SOILS

Remove it from the bath, allow it to settle for about three minutes, and decant it through a Gooch crucible containing a thin felt of washed and ignited asbestos, using suction.

To the residue in the dish add a second mixture of 30 cc. water, 10 cc. 2.5 per cent HCl and 10 cc. 2.5 per cent HF. Digest again on the water bath for exactly five minutes, allow to settle, and decant through the Gooch crucible.

Repeat the foregoing digestions and decantations four times more, making six separate digestions in all. Then transfer the soil residue completely to the crucible, using hot water and a policeman. Wash thoroughly with hot water, using suction.

Dry the crucible and contents over night in the electric oven at 95° to 100°C. Cool in a desiccator and weigh. Ignite the crucible and contents at low redness for one hour. Cool and weigh. The loss in weight resulting from ignition represents organic matter.

Too high results are probable, because of incomplete removal of the hydrated colloids of the soil. It appears unlikely that the percentages of organic matter reported are too low.

The accompanying distribution diagram summarizes the results. The mean nitrogen content is 0.31 ± 0.004 per cent, and that of the organic matter is 3.75 ± 0.03 per cent. The coefficient of correlation between nitrogen and organic matter is +0.74. Assuming a factor of 1.72 for carbon to organic matter, we get an average carbon percentage of 2.18 and a carbon-nitrogen ratio of 7 to 1. The 10 to 1 line has been drawn across the diagram and almost all of the samples are shown to be too rich in nitrogen to conform to that value.

There was a tendency for the very dry and very wet lands to run somewhat low in organic matter. Some of the driest districts have an annual rainfall well below 20 inches, which is rather dry in a subtropical region. In such places the organic matter is frequently less than 2 per cent. Some of the wettest districts have an excessive leaching of the soil, with resulting soils of low fertility and pH values around 4.0. The districts of moderate rainfall tend to have soils which are well provided with organic matter.

It is clear that the nitrogen content of our soils does not agree at all with the data presented by Jenny. To be consistent, this average should be less than 0.1 per cent, whereas it is three times that. On the basis of soil nitrogen, Hawaii belongs just south of the Canadian boundary instead of south of the Tropic of Cancer.

A number of years ago, Kelley (3) emphasized the inert character of the nitrogen in the uncultivated Hawaiian soils. He attributed this to lack of aeration. The cultivated soils of the pineapple industry receive an unusually thorough mechanical preparation; six to ten plowings extending over a period of one or two years are customary. Nitrification of added fertilizers takes place rapidly in these cultivated lands. Thoroughly prepared lands, before being fertilized and planted, sometimes show nitrate nitrogen contents between 50 and 100 p.p.m., and commonly over 20 p.p.m. A careful check on the organic matter of a number of virgin soils which were broken up for pineapples has shown a drop in this component with a tendency for the soils to become stable at some percentage between 3 and 4.

Whatever may be the reasons, it seems fairly evident that our Hawaiian soils are rich in nitrogen as compared with the southern states, and that their organic matter contains a higher percentage of nitrogen than the usual run of soils of the temperate zone. This latter observation is consistent with the tendency for the carbon-nitrogen ratio to become narrower with increasing mean annual temperature as brought out by Jenny (2).

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THE OXIDATION OF PYRITE AND SULFUR AS INFLUENCED BY LIME AND MAGNESIA—A 12-YEAR LYSIMETER STUDY

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In previous lysimeter studies at this station it was found that different forms and amounts of lime and magnesia exerted divergent effects upon the leachings of sulfates that were derived from the soil and rainfall (4, 8, 9). In the early period of a subsequent experiment a similar divergence was obtained when sulfur additions were made in three forms (10). Further studies developed the reasons for the fixation of the sulfate radical by CaO (5, 6). The present contribution gives the results obtained in a 12-year lysimeter study of the oxidation of pyrite and elemental sulfur with ferrous sulfate control, as influenced by lime and magnesia. The changes that transpired in the soil are considered on the basis of: the recovery of sulfur as leached sulfate; the outgo of calcium, magnesium, and potassium; and the outgo of nitrates.

EXPERIMENTAL

The project was begun August 3, 1917 and terminated August 3, 1929. The average annual rainfall during that period was 51 inches. A soil of the Hagerstown series, a brown, fairly fertile loam of a slightly sandy phase, was used without subsoil. The soil had a total S content of 0.0326 per cent and gave an electrometrical pH value of 6.27 in a 1–10 suspension after one hour. As determined by $Na_2O_2-Na_2CO_3$ fusion, the total CaO and MgO contents of the soil were 0.217 per cent and 0.398 per cent, or $CaCO_3$-equivalences of 0.388 per cent and 0.995 per cent, respectively.

The sulfur additions—ferrous sulfate, pyrite, and elemental sulfur—were made at the constant rate of 1,000 pounds of S to 2,000,000 pounds of soil. The sulfur contents of the three materials were 18.15 per cent, 51.95 per cent, and 99.89 per cent, respectively. Pyrite was included, on the supposition that this cheap mineral would oxidize slowly and thus insure a uniform supply of sulfates. The ferrous sulfate was included to eliminate the effect of any additive base, to parallel the effect of iron in the pyrite, and to provide an absolute check on the outgo of the sulfate radical, instead of depending upon theoretical computations.

Each sulfur carrier was used alone and with lime and magnesia at the CaO-equivalent rates of 1 ton and 32 tons. The actual acidity of the ferrous sulfate, and that possible from the full oxidation of the pyrite and sulfur, was equivalent

to 1,750 pounds of CaO. The 1-ton lime and magnesia treatments were therefore supplemented by this amount. This supplement of CaO or MgO was not neutralized with uniform rapidity. The difference between the immediate action of the ferrous sulfate and the slower action of the generated sulfate radical was cared for by the use of both 2,000-pound and 3,750-pound controls. Limestone and dolomite of 100-mesh fineness, and at the CaO-equivalent rate of 2,000 pounds, or 3,570 pounds of $CaCO_3$, were also included in the group of controls.

SULFATE OUTGO

The sulfur additions, increments, and recoveries are expressed throughout as pounds of S to 2,000,000 pounds of soil. The percolated sulfates are considered as a measure of the speed and ultimate extent of the oxidation of pyrite and elemental sulfur. No other record of the use of either sulfate or pyrite in lysimeter studies has been found. Recently, however, ferrous sulfate was used as a soil amendment by Kelley and Arny (3) in extensive laboratory-controlled plat studies with alkali soils, and the oxidation of heavy pyrite additions in soil cultures was studied by Rudolfs (11).

No-sulfur-addition group. The data of the first group in table 1 show that all of the six liming treatments produced an increase in the outgo of sulfates. In general, the increases were accounted for during the first two years. The effects of the four 2,000-pound additions were comparable. The effects of the 1,750-pound supplements of CaO and MgO were definite, though not extensive. It therefore appears that the variations in the rapidity with which the 1,750-pound supplements were neutralized did not constitute an important factor in the sulfate outgo from the soil itself.

The relation between increment of sulfates from rainwaters and the outgo of sulfates from the no-sulfur control group is shown in table 2. There was no actual loss of sulfates from the untreated soil through leaching, since the outgo from the control was only 78.8 per cent of that brought down by rain. This relationship between increment and outgo was also found recently for a similar soil by Ellett and Hill (2). Neither of the limestones, nor the equivalent oxide treatments, produced a sulfate leaching equal to that derived from the rain, 514 pounds. The respective losses from the 3,750-pound lime and magnesia additions exceeded the sulfates derived from rainwater by only two per cent and four per cent. Increases in outgo of sulfates, as a result of liming, were also found by Ellett and Hill (2) for those soils that were not underlaid by subsoil. Economic liming might be considered as causing a decrease in the capacity of the soil to retain sulfates. In view of the immediate enhancement in the sulfate content of the percolates, however, it is more probable that oxidation of the supply of organic sulfur in the soil was stimulated by the liming.

Ferrous sulfate group. The ferrous sulfate control gave a large sulfate outgo during the first year. This outgo was, however, only a fraction of the greater losses induced by the 1-ton supplements of the two oxides, and only 53 per cent

of the outgo from the heavy MgO addition. The 32-ton addition of burnt lime resulted in the formation of the compound $3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 33\,H_2O$, which is insoluble during the persistence of $Ca(OH)_2$; hence the sulfate outgo from the heavily limed ferrous sulfate addition was greatly retarded (6).

TABLE 1

The 12-year outgo of sulfate sulfur derived from 1,000-pound S equivalence additions of ferrous sulphate, pyrite and sulfur to a loam soil, as influenced by lime and magnesia supplements

TANK NUMBER	LIME OR MAGNESIA ADDITIONS		SULFUR ADDITION	ANNUAL OUTGO OF S IN POUNDS FROM 2,000,000 POUNDS OF SOIL												
	Form	Rate*		First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth	Ninth	Tenth	Eleventh	Twelfth	Total 12 years
50	None	.....	None	18	37	47	41	34	32	18	19	37	41	37	44	405
51	L.S.	2,000	None	58	55	44	41	35	30	23	24	41	40	42	39	472
52	Dol.	2,000	None	62	56	46	41	37	29	24	30	48	46	46	42	507
53	CaO	2,000	None	62	59	48	45	34	32	23	27	43	44	43	43	503
54	CaO	3,750	None	81	56	49	40	35	30	26	30	46	42	43	47	525
55	MgO	2,000	None	63	53	47	43	35	33	25	28	40	44	42	41	494
56	MgO	3,750	None	94	57	51	43	34	31	26	30	40	41	45	44	536
57	None	.....	$FeSO_4$	534	180	109	68	42	44	23	26	37	55	40	50	1,208
58	CaO	3,750	$FeSO_4$	829	173	74	50	38	35	24	27	45	47	42	43	1,427
59	MgO	3,750	$FeSO_4$	940	129	61	46	37	34	26	31	42	47	47	44	1,484
60	CaO	32T	$FeSO_4$	82	178	264	221	147	39	31	33	49	45	49	47	1,185
61	MgO	32T	$FeSO_4$	1,007	184	55	41	34	34	23	27	45	49	39	48	1,586
62	None	.....	Pyrite	183	279	206	116	87	62	30	34	52	66	43	57	1,215
63	CaO	3,750	Pyrite	189	363	154	120	92	75	51	53	67	66	58	56	1,344
64	MgO	3,750	Pyrite	184	255	133	84	56	48	38	42	57	56	59	52	1,064
65	CaO	32T	Pyrite	32	67	97	132	87	130	114	161	111	94	85	77	1,187
66	MgO	32T	Pyrite	166	107	79	54	50	65	40	42	59	61	52	68	843
67	None	.....	Sulfur	507	211	118	70	50	43	25	25	46	55	42	50	1,242
68	CaO	3,750	Sulfur	734	236	78	51	38	31	23	29	42	42	43	42	1,389
69	MgO	3,750	Sulfur	817	219	70	50	37	34	26	29	40	46	48	43	1,459
70	CaO	32T	Sulfur	89	205	263	218	117	47	35	34	48	47	52	41	1,196
71	MgO	32T	Sulfur	426	608	117	51	37	35	22	26	48	47	39	47	1,503
Rainfall.....*inches*				41	51	55	56	51	55	44	35	51	59	55	58	514
Average.....																51

* Pounds, or tons, CaO = to 2,000,000 pounds of soil, moisture-free basis.

The sulfate outgo from the ferrous sulfate control decreased decidedly after the first year; the difference between the loss from it and the loss from the untreated soil at the end of the third year was 721 pounds, as compared with 803 pounds after 12 years. Thus, in spite of 12 years of leaching, there was a re-

tention of 20 per cent of the sulfur added in the ferrous sulfate control. This indicates that insoluble sulfate compounds were formed in the soil. On the other hand, it is possible that there was a loss of sulfur as a result of reduction in the acid soil. No ferrous sulfate appeared in the early leachings from any of the ferrous sulfate tanks. The increase in the sulfate radical was accounted for by enhancements in leachings of calcium and magnesium. This does not confirm the viewpoint of Van Bemmelen (12) that the sulfuric acid radical combines with iron in the soil to protect the alkaline-earth bases against solvent action and leaching. It does accord, however, with the conclusions of Kelley and Arny (3) relative to the reactions that ensue between ferrous sulfate and exchangeable calcium and magnesium.

When the sulfate losses from the two light additions of oxides and the heavy addition of magnesia are corrected for outgo from the untreated soil, the recoveries are more than equal to the sulfate content of the ferrous sulfate addition.

Table 1 shows the more rapid outgo of magnesium sulfate. After the third year, however, the outgo for the two MgO additions and the 1-ton CaO addition was almost identical. The initial sulfate fixation by the heavy lime treatment was not permanent and the outgo for sulfate alone and for sulfate plus 32 tons of lime, was practically identical during the last seven years. The common-ion effect is not a potent factor during the period subsequent to the conversion of the hydrated lime into calcium carbonate.

Sulfur group. Because of its similarity to the sulfate group, and its dissimilarity to the pyrite series, the elemental sulfur group will next be considered. At the end of the first year the sulfate outgo from the unlimed sulfur addition was only 11 pounds less than one half the amount added. The outgo from the sulfur control was practically the same as that from the ferrous sulfate control by periods and for the 12-year total. Even without liming, the oxidation of the sulfur kept pace with the removal through leaching. The 1-ton additions of lime and magnesia caused distinct acceleration in sulfur oxidation and gave net sulfate recoveries of 91.5 per cent and 98.1 per cent, respectively, during the first two years. The heavy lime addition caused the same marked decrease in sulfate outgo that was found for ferrous sulfate. It is most probable that the intense alkalinity produced by the heavy addition of lime was inhibitive to the biological oxidation of elemental sulfur. Nevertheless, it is not proved that the heavy lime additions did produce this effect, for had sulfates been present as they were in the ferrous sulfate series, they would not have come out in the percolates during the persistence of the $Ca(OH)_2$. The explanation for this chemical phenomenon has been given in the discussion of the ferrous sulfate data.

The first annual outgo of sulfates from the sulfur addition with 32 tons of magnesia amounted to only 84 per cent of that obtained from the sulfur alone, and only 42.3 per cent of the 1,007-pound outgo from the corresponding ferrous sulfate addition. At the end of two years, however, the heavy magnesia

treatment gave a net sulfate recovery of 97.9 per cent of the sulfur addition. Hence, though delayed in starting, the sulfate recovery from the heavier magnesia addition caught up with that from each oxide at the lighter rate, and ultimately was the largest of the sulfur group. Data in table 1 show that, at the 1-ton rate, both oxides gave a full sulfur recovery, but there was a disparity of 31.2 per cent between the excess recovery from 32 tons of magnesia and the minus value found for the corresponding addition of burnt lime.

Since the same heavy sulfate outgo was produced from this soil by the 32-ton additions without any added sulfur (8, 9), it would appear that the oxidation of elemental and native organic sulfur was induced by the same, or a similar, organism.

Pyrite group. In this group the oxidation process was immediate and positive, save for the 32-ton addition of burnt lime. Nevertheless, the respective generations of sulfates were not nearly so rapid as in the sulfur group. In table 1 it is shown that no pyrite addition gave a 100 per cent recovery, and only in the case of the 1-ton CaO treatment was the enhanced outgo greater than that from the unsupplemented pyrite. The descending order in sulfate outgo from heavy magnesia, light magnesia, light lime, control, and heavy lime that was found for both the ferrous sulfate and elemental sulfur, was changed materially in the pyrite group. The order of outgo from the first four years was, pyrite plus one ton of CaO, pyrite alone, and pyrite plus one ton of MgO, with respective losses of 826, 784, and 656 pounds. This order did not hold, however, for the full 12-year period. The greatest total loss—1,344 pounds for the 1-ton CaO addition—was followed by an outgo of 1,215 pounds from the pyrite alone, but the ultimate loss induced by 32 tons of CaO was greater than the outgo caused by the light addition of magnesia. In decided contrast to the ferrous sulfate and elemental sulfur groups, the minimum loss of sulfates came from the 32-ton addition of magnesia in spite of the initial lag in the outgo from the heavy lime addition. The minimum sulfate outgo from the pyrite and heavy magnesium oxide cannot be explained by assuming that *magnesium sulfite* was formed through reaction between SO_2 and hydrated magnesium oxide, for this salt is readily soluble in water, and if leached it would have been converted to magnesium sulfate during the analytical procedure. The data of the ferrous sulfate and elemental sulfur groups show that magnesium sulfate would have come out, had it been present. Hence, it is evident that the heavy magnesia additions had a depressive effect upon the production of sulfates from the pyrite. If it be assumed that the pyrite was oxidized mainly through bacterial action, it follows that the organism that effected oxidation of the pyrite was different from that which caused oxidation of the elemental sulfur.

The oxidation of pyrite may be effected in part by bacteria, as was concluded by Rudolfs (11); nevertheless, the mineral sulfide readily undergoes a purely chemical change into ferrous sulfate, as indicated by the equation,

$$FeS_2 + 3O_2 = FeSO_4 + SO_2$$

Distinct evidence of SO_2 is obtained from samples of the finely ground material that have been stored in corked bottles. We have confirmed the observations of Allen and Johnston (1) to the effect that considerable quantities of ferrous sulfate are generated when pyrite is ground to obtain an analytical charge. It is quite probable that the generation of sulfates from the added pyrite was therefore due in considerable part to purely chemical action.

The rates of cumulative outgo of sulfate-sulfur from 1,000-pound S-equivalent additions of pyrite with and without lime and magnesia (table 1) are materially different from those resulting from the addition of elemental sulfur and ferrous sulfate. The total recovery of 1,215 pounds from the pyrite control is in remarkable concordance with the 1,208-pound and 1,242-pound recoveries from the ferrous sulfate, and sulfur controls, respectively. A similar concordance was found in the yields of 1,185, 1,187, and 1,196 pounds from the same three materials with the 32-ton CaO supplement. Only in the case

TABLE 2

Total sulfate S outgo from soil without sulfur increment except through rainfall

SULFATE S PER 2,000,000 POUNDS OF SOIL, MOISTURE-FREE BASIS	IN PERCOLATES FROM SOIL WITH ADDITIONS OF						
	No treatment	100-mesh, 2,000-pounds CaO-Equivalent		Burnt lime		Burnt magnesia	
		Limestone	Dolomite	2,000-lb. rate	3,750-lb. rate	2,000-lb. "	3,750-lb. "
Actual outgo.....*pounds*	405	472	507	503	525	494	536
Increase over control.....*pounds*	....	67	102	98	120	89	131
Increase over control.....*per cent*	....	16.5	25.2	24.2	29.6	22.0	32.3
Outgo, as per cent of rainfall increment..	78.8	91.8	98.6	97.9	102.1	96.1	104.3

of the pyrite plus 32 tons of CaO, with its early inhibitive action, is there to be found an outgo of sulfates that is not in harmony with the recoveries from the other treatments during the last 5-year period, and it is evident that a state of virtual equilibrium between sulfur supply and sulfate outgo has been reached.

OUTGO OF CALCIUM, MAGNESIUM, AND POTASSIUM

Calcium-magnesium outgo

Each calcium and magnesium outgo is expressed as pounds $CaCO_3$-equivalent for each 2,000,000 pounds of soil.

Control group. The data of table 3 show practically the same outgo of calcium for the 2,000-pound equivalences of high-calcic lime and limestone. A larger outgo came from the 3,750-pound CaO addition. This larger outgo was evident in each of the 12 annual periods and aggregated 1,227 pounds of $CaCO_3$-equivalence. By an increase of seven-eighths of the lime added, the enhanced outgo was 2.66 times the actual loss from the 1-ton CaO addition. Each increment of magnesium depressed the outgo of calcium, and the 3,750-

pound MgO addition was more repressive than the 2,000-pound treatment. This repressive effect was exerted by the magnesium content of the dolomite, as well as the oxides of magnesium, as has been noted and explained in a previous contribution (7).

The magnesium leachings from the high-calcic additions were uniformly lower than the magnesium outgo from the untreated soil (fig. 1). The dolomite gave a magnesium outgo practically double that from the untreated soil.

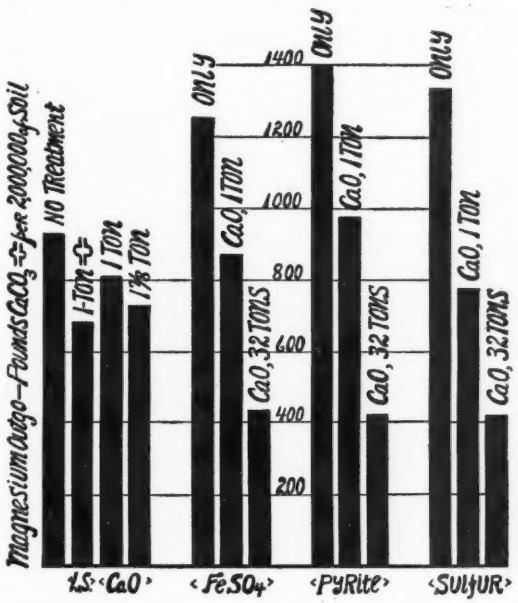

FIG. 1. THE REPRESSIVE EFFECT OF UNSUPPLEMENTED ADDITIONS OF LIMESTONE AND BURNT LIME UPON THE OUTGO OF NATIVE SOIL MAGNESIUM; THE ENHANCEMENT IN OUTGO OF NATIVE MAGNESIUM INDUCED BY UNSUPPLEMENTED ADDITIONS OF FERROUS SULFATE, PYRITE, AND ELEMENTAL SULFUR; AND THE DEPRESSED OUTGO OF NATIVE MAGNESIUM FROM FERROUS SULFATE, PYRITE, AND ELEMENTAL SULFUR WHEN SUPPLEMENTED WITH BURNT LIME AT TWO RATES

Since the 100-mesh dolomite addition had been absorbed before the end of the first year, this enhancement is to be attributed to the greater hydrolytic disintegration of the magnesium absorption complex. The complete removal of the absorbed magnesium would account for about 87 per cent of the magnesium outgo. The enhancement in the magnesium outgo from the 3,750-pound MgO addition was exactly 1.875 times that from the 1-ton addition.

The persistence of liming materials in the soil is considered in the summaries given in table 4. The total calcium plus magnesium outgo from the 2,000-pound CaO-equivalences of burnt lime, limestone, and dolomite did not differ materially, although that from the dolomite was the greatest. The maximum

TABLE 3

The 12-year outgo of calcium from lime and magnesia additions to a loam soil, as influenced by 1,000-pound sulfur additions in the forms of ferrous sulfate, pyrite, and pulverized sulfur

TANK NUMBER	LIME OR MAGNESIA ADDITIONS		SULFUR ADDITIONS	ANNUAL OUTGO OF CALCIUM AS $CaCO_3$ IN POUNDS TO 2,000,000 POUNDS OF SOIL												
	Form	Rate*		First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth	Ninth	Tenth	Eleventh	Twelfth	Total 12 years
50	None	.....	None	292	248	234	260	188	143	108	89	223	174	195	171	2,325
51	L.S.	2,000	None	370	406	336	351	201	156	148	128	282	204	235	209	3,026
52	Dol.	2,000	None	230	273	227	219	166	132	87	83	213	171	177	122	2,100
53	CaO	2,000	None	406	408	278	371	226	179	150	149	289	224	231	167	3,078
54	CaO	3,750	None	697	587	477	483	293	234	170	167	366	274	291	266	4,305
55	MgO	2,000	None	155	147	166	161	111	98	50	61	128	100	125	98	1,400
56	MgO	3,750	None	155	143	166	160	96	67	42	42	108	77	90	102	1,248
57	None	.....	$FeSO_4$	1,348	611	374	278	172	116	76	87	169	146	137	132	3,646
58	CaO	3,750	$FeSO_4$	2,607	718	351	338	205	179	151	155	311	237	229	220	5,701
59	MgO	3,750	$FeSO_4$	582	139	121	132	89	46	45	48	101	83	88	76	1,550
60	CaO	32T	$FeSO_4$	3,801	1,653	1,863	1,350	1,229	833	500	552	818	820	882	981	15,282
61	MgO	32T	$FeSO_4$	79	60	103	94	60	43	31	37	63	78	97	108	853
62	None	.....	Pyrite	533	896	615	381	308	159	105	110	207	168	141	151	3,774
63	CaO	3,750	Pyrite	865	1,111	643	535	380	298	215	171	393	298	307	280	5,496
64	MgO	3,750	Pyrite	297	242	161	159	101	65	56	47	110	104	104	101	1,547
65	CaO	32T	Pyrite	4,951	1,724	1,276	1,503	1,161	1,160	954	868	979	933	928	1,116	17,553
66	MgO	32T	Pyrite	75	63	88	92	56	42	35	39	57	78	109	127	861

67	None	.....	Sulfur	1,280	617	400	306	186	128	89	103	190	149	140	137	3,725
68	CaO	3,750	Sulfur	2,310	907	384	345	234	179	137	142	296	241	230	212	5,617
69	MgO	3,750	Sulfur	526	214	245	189	119	83	72	67	124	95	109	113	1,956
70	CaO	32T	Sulfur	4,163	1,973	1,772	1,864	1,342	1,050	660	612	858	859	1,001	1,115	17,269
71	MgO	32T	Sulfur	55	65	72	102	59	40	35	33	54	79	109	136	839
Rainfall content.....				36	48	.....	.....	.....	29	45	31	21	30	53	40	444†
Rainfall.....*inches*				41	51	55	56	51	55	44	35	51	59	55	58	611
Average.....																51

* Pounds or tons CaO = for each 2,000,000 pounds of soil, moisture-free basis.

† On the basis of an average of 9 of the 12 years.

enhancement in outgo, however, was equivalent to only 18.1 per cent of the addition. A good part of the outgo of Ca + Mg may be attributed to the calcium and magnesium that is added through rainfall—computed to be 808 pounds, or 25 per cent of the loss from the untreated soil. If the determined outgo of 3,257 pounds from the untreated soil be corrected for the 808-pound rainfall increment, the net loss is 2,449 pounds, or 204 pounds yearly. In each comparison of CaO and MgO the greater solubility of the magnesium complex was responsible for a consistently greater periodic and total Ca + Mg outgo, in which was masked the decidedly repressive effect of magnesium upon calcium outgo (7).

The outgo from the limed soils may be logically assumed to have been derived mainly from the freshly formed and more soluble absorption complexes. If it be true that the entire calcium-magnesium outgo was due to the liming materials, and that the original calcium-magnesium content continued in the original state, it would mean that, as an average, 92.3 per cent of the added materials—

TABLE 4

The conservation of Ca + Mg from single economic additions of burnt lime and 100-mesh limestone and dolomite, as measured by the outgo over a 12-year period—terms of $CaCO_3$ = per 2,000,000 pounds of soil*

OUTGO OF Ca + Mg, AS $CaCO_3$ =	FROM UNTREATED SOIL	FROM CaO ADDITION	FROM LIMESTONE ADDITION	FROM DOLOMITE ADDITION
Actual.....*pounds*	3,257	3,892	3,712	3,934
Increase.....*pounds*	.....	635	455	677
Increase.....*per cent* of addition	.....	17.8	12.7	18.1

* 2,000-pound CaO =, or 3,570-pound $CaCO_3$ =.

burnt lime, limestone, and dolomite—had been lost by leaching during the 12-year period. To a certain extent this may be true, but it could not be the absolute condition in the case of the burnt lime and limestone, because the leached magnesium was derived almost entirely from the soil's original supply, plus precipitation, in both limed and unlimed soil, in spite of the "reciprocally repressive" effect. If the outgo of magnesium from the untreated soil and that from the limed soil be considered as identical, and all of the calcium loss be considered as derived from the added lime, then the recovery of calcium from the burnt lime would be 86 per cent of the addition. A similar calculation would give an 85 per cent loss from the 100-mesh limestone. Since the dolomite gave a calcium outgo of less than that from the untreated soil, the effect exerted by absorbed magnesium was probably to conserve the original calcium; therefore, the calcium outgo from the dolomite treatment may be attributed in most part to the calcium content of the dolomite.

Sulfur-addition groups. The relationships found for the total outgo of both

calcium and magnesium from the triplicated additions of lime and magnesia are such that the three sulfur groups may well be considered together. The total enhancement in calcium outgo was comparable for the three unsupplemented sulfur materials. It is interesting to observe, however, that the pyrite addition gave an outgo of calcium in excess of that from the ferrous sulfate and that from sulfur during each of the last 11 annual periods. The order of calcium outgo was the same for each sulfur material—heavy lime, light lime, sulfur material, light magnesia, and heavy magnesia additions. In like manner there was a constant order of magnesium outgo for all three groups—heavy magnesia, light magnesia, sulfur material, light lime, and heavy lime additions. On the whole, the total calcium, or magnesium, outgo from each liming material was uniform, irrespective of the form in which sulfur was added. The one notable exception was the smaller outgo of calcium from the heavy addition of burnt lime with ferrous sulfate, as compared with larger and concordant loses from the heavy addition with supplements of sulfur and pyrite.

A previous paper (7) shows the repressive effect that magnesium exerted upon calcium outgo in the unsulfured soil. It also shows that the unsupplemented sulfur materials caused a uniform increase in the outgo of calcium from the native supplies. It is strikingly evident that the magnesic additions protected the native calcium against the action of the sulfate radical, so that the calcium outgo from each sulfur material with a magnesia supplement was less than that from the untreated soil. In this respect the heavier additions of magnesia were consistently more effective. This means that even the 1-ton MgO addition prevented any interchange between the exchangeable calcium of the soil and the magnesium content of the 3,750-pound magnesium sulfate increments. In figure 1 is shown the corresponding repressive and protective tendency of liming materials upon magnesium outgo. The single exception found was the pyrite with the 1-ton addition of burnt lime. In this case, where the sulfates were generated slowly over a long period, the magnesium outgo was approximately that from the untreated soil.

Potassium outgo

The potassium outgo may be discussed briefly as a whole. All of the light unsupplemented, calcic and magnesic materials caused some depression in the total outgo of potassium (table 5). Neither of the unsupplemented sulfur-carriers induced a positive liberation of potassium in the acid soil, in spite of the bathing action of neutral salts of calcium and magnesium that were supplied immediately in one case and progressively in two cases. When used with the three sulfur materials, each addition of lime and of magnesia caused a definite decrease in potash outgo, the heavier additions being consistently more effective. There is a remarkable agreement in the potassium leachings obtained from each liming material, at each rate, when used with the three sulfur materials.

OUTGO OF NITRATE

The annual and total losses of nitrate nitrogen are given in table 6. Five of the six liming treatments without sulfur caused some increase in the outgo of nitrogen. The losses induced by the 3,750-pound additions were somewhat

TABLE 5

The influence of various forms and amounts of calcic and magnesic materials and three sulfur supplements upon the outgo of the native potash of a loam soil over a 12-year period

TANK NUMBER	LIME OR MAGNESIA ADDITIONS		SULFUR ADDITION†	ANNUAL OUTGO OF K IN POUNDS, FROM 2,000,000 POUNDS OF SOIL												
	Form	Rate*		First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth	Ninth	Tenth	Eleventh	Twelfth	Total 12 years
50	None	.....	None	11.8	8.4	12.7	7.0	6.2	5.5	3.6	6.3	11.5	10.6	8.3	9.0	101
51	L.S.	2,000	None	9.0	7.0	9.0	9.5	7.8	3.1	4.0	6.3	10.1	13.5	6.3	9.0	95
52	Dol.	2,000	None	7.4	5.5	9.6	8.5	4.1	3.8	4.4	4.8	6.8	5.0	12.4	6.7	79
53	CaO	2,000	None	9.2	6.7	10.2	11.2	4.7	4.5	4.3	6.2	8.7	4.9	11.4	4.8	87
54	CaO	3,750	None	5.6	6.8	11.6	7.5	4.1	3.6	2.4	5.6	9.9	13.1	10.1	7.0	87
55	MgO	2,000	None	7.7	6.1	8.5	5.1	4.4	2.5	4.5	6.7	9.8	7.0	4.0	6.3	73
56	MgO	3,750	None	8.5	6.3	9.8	8.9	4.2	3.2	4.2	8.6	10.1	5.0	4.8	9.0	83
57	None	.....	$FeSO_4$	14.8	10.2	9.6	12.2	6.6	5.4	4.0	5.8	6.8	9.4	5.4	9.0	99
58	CaO	3,750	$FeSO_4$	6.0	7.3	10.2	7.7	4.5	2.9	3.0	3.1	9.7	8.2	5.2	6.2	74
59	MgO	3,750	$FeSO_4$	5.3	5.7	15.4	8.3	3.3	3.5	4.7	5.0	10.1	7.6	4.3	5.3	79
60	CaO	32T	$FeSO_4$	5.4	5.3	14.6	5.5	4.9	2.3	3.0	2.2	9.8	10.6	5.4	7.9	77
61	MgO	32T	$FeSO_4$	10.3	4.4	6.9	4.2	2.3	0.6	3.7	12.6	7.8	5.5	3.3	7.0	69
62	None	.....	Pyrite	11.6	10.6	11.3	10.8	6.6	5.3	2.2	4.0	14.3	6.8	8.2	10.6	102
63	CaO	3,750	Pyrite	6.5	10.8	8.1	7.5	5.2	2.8	2.4	2.8	8.0	4.8	4.0	8.4	71
64	MgO	3,750	Pyrite	8.7	6.0	9.5	3.5	2.5	2.2	3.3	5.1	12.4	4.9	3.5	4.9	67
65	CaO	32T	Pyrite	6.4	7.0	9.6	8.8	5.1	2.9	4.0	2.6	7.5	7.0	3.7	5.8	70
66	MgO	32T	Pyrite	8.2	4.6	7.6	4.5	2.4	0.8	4.3	2.5	9.6	4.9	3.4	10.0	63
67	None	.....	Sulfur	15.1	11.1	14.7	9.4	5.3	5.3	4.4	8.6	8.8	8.3	6.7	7.2	105
68	CaO	3,750	Sulfur	6.6	10.7	10.4	8.9	5.2	1.6	3.9	3.6	10.9	5.5	2.9	6.9	77
69	MgO	3,750	Sulfur	12.7	7.7	8.6	7.6	3.5	1.7	4.0	3.6	9.1	6.2	3.2	6.2	74
70	CaO	32T	Sulfur	8.4	6.5	7.7	11.0	6.0	3.2	3.3	2.9	7.8	5.2	6.2	7.2	75
71	MgO	32T	Sulfur	8.0	3.5	7.4	3.6	2.3	1.5	3.1	6.0	7.4	4.9	2.8	8.9	59
Rainfall..... *inches*				41	51	55	56	51	55	44	35	51	59	55	58	611
Average.....																51

* Pounds or tons, CaO = to each 2,000,000 pounds of soil, moisture-free basis.

† Constant rate of 1,000 pounds of S to 2,000,000 pounds of soil, moisture-free basis.

greater than those from the 2,000-pound CaO-equivalent additions, and magnesia tended to give a greater outgo than did lime.

The outgo from each unsupplemented sulfur material was less than that from the untreated soil. The ferrous sulfate control gave the minimum for

the 22 tanks. Each light addition of lime and magnesia gave an increased outgo of nitrates, when used with each of the three sulfur materials. In each of the pairs of CaO and MgO at the 1-ton-plus rate, the magnesia gave the greater outgo. A reverse relationship was obtained in a similar com-

TABLE 6

The 12-year outgo of nitrate nitrogen from a loam soil as influenced by 1,000-pound S-equivalent additions of ferrous sulfate, pyrite, and sulfur, with and without lime and magnesia

TANK NUMBER	LIME OR MAGNESIA ADDITIONS		SULFUR ADDITIONS	ANNUAL OUTGO OF NITRATE N IN POUNDS, FROM 2,000,000 POUNDS OF SOIL												
	Form	Rate*		First	Second	Third	Fourth	Fifth	Sixth	Seventh	Eighth	Ninth	Tenth	Eleventh	Twelfth	Total 12 years
50	None	.....	None	24	49	15	23	20	17	18	8	34	11	18	16	253
51	L.S.	2,000	None	21	63	27	33	14	13	21	11	30	14	17	20	284
52	Dol.	2,000	None	20	54	20	28	14	9	13	8	32	5	15	13	231
53	CaO	2,000	None	24	58	25	29	15	19	20	13	33	5	14	13	268
54	CaO	3,750	None	40	72	35	19	16	17	14	11	34	13	21	20	312
55	MgO	2,000	None	34	55	27	25	18	20	16	13	31	7	19	17	282
56	MgO	3,750	None	41	66	35	39	16	16	17	12	32	5	20	23	322
57	None	.....	$FeSO_4$	13	37	16	17	12	10	12	11	31	9	19	11	198
58	CaO	3,750	$FeSO_4$	22	49	25	23	19	14	20	14	33	8	17	16	260
59	MgO	3,750	$FeSO_4$	23	46	30	28	22	22	18	18	35	8	16	18	284
60	CaO	32T	$FeSO_4$	15	129	111	59	32	18	11	15	40	11	24	17	482
61	MgO	32T	$FeSO_4$	26	145	70	35	25	27	20	23	29	5	26	20	451
62	None	.....	Pyrite	17	28	17	20	24	19	14	17	30	7	18	16	227
63	CaO	3,750	Pyrite	46	55	26	28	15	24	14	11	37	5	16	14	291
64	MgO	3,750	Pyrite	51	61	27	30	18	21	16	14	38	5	17	16	314
65	CaO	32T	Pyrite	24	125	108	99	49	27	17	12	34	7	21	19	542
66	MgO	32T	Pyrite	35	106	46	32	24	44	26	22	30	5	23	20	413
67	None	.....	Sulfur	13	34	16	20	16	17	16	15	36	8	17	12	220
68	CaO	3,750	Sulfur	22	45	24	27	16	16	16	16	35	5	23	15	260
69	MgO	3,750	Sulfur	30	52	21	28	18	18	15	13	36	6	20	15	272
70	CaO	32T	Sulfur	18	136	75	103	49	35	18	14	38	5	24	16	531
71	MgO	32T	Sulfur	22	141	49	40	26	37	26	20	30	5	25	28	449
Rainfall..... *inches*				41	51	55	56	51	55	44	35	51	59	55	58	

* Pounds or tons, to each 2,000,000 pounds of soil, moisture-free basis.

parison of the 32-ton additions. The intensive alkalinity of the heavy lime treatment produced a partial sterility during most of the initial year; but during the second, third, and fourth years the recovery was very marked. During the first year, two of the first four percolate collections from each 32-ton addition of lime were *devoid* of nitrates. In each case the amount of

nitrogen that passed out between the beginning of the experiment, August 3, 1917, and April 22, 1918, was less than 1 pound. The nitrate-nitrogen leached out between April 22, and the first birthday, August 3, 1918, therefore amounted to approximately 14, 23, and 17 pounds for the 32-ton CaO additions with ferrous sulfate, pyrite, and sulfur, respectively. The initial effect of the MgO was not repressive, nor did it show a subsequent accelerative effect as great as that shown by the heavy lime addition. It may be concluded that a sulfur addition will be apt to cause a reduction in the generation of nitrates, but that this effect is eliminated when moderate additions of lime and magnesia are also made.

SUMMARY

The oxidation of 1,000-pound sulfur additions of pyrite and elemental sulfur, as influenced by lime and magnesia, was studied with ferrous sulfate control in a 12-year lysimeter experiment without subsoil, through determination of the outgo of sulfates, calcium, magnesium, potassium, and nitrates.

Burnt lime, magnesia, limestone, and dolomite gave increases in sulfate outgo, but no 2,000-pound calcium oxide equivalent addition gave a sulfate outgo equal to the sulfates supplied by rainfall.

Sulfate outgo from ferrous sulfate additions corresponded to that from sulfur in the order of heavy magnesia, light magnesia, light lime, sulfur material alone, and heavy lime. The order of outgo from the pyrite was light lime, pyrite alone, heavy lime, light magnesia, and heavy magnesia. The divergent effect of lime and magnesia indicated that the organism that induced oxidation of organic soil sulfur and elemental sulfur was different from the one that produced sulfates from pyrite. The chemical oxidation of pyrite was also considered.

Complete recoveries of the sulfate radical were obtained from the ferrous sulfate additions with light calcium and magnesium oxides and heavy magnesium oxide supplements, but not from the sulfate alone or sulfate plus 32 tons of lime. Complete sulfate-equivalences of the elemental sulfur were obtained from the two megnesia supplements, but not from the sulfur control, or the sulfur addition with lime supplements. Complete recovery was not obtained from any one of the five pyrite additions. The formation of insoluble sulfates and the reduction of sulfates are considered as factors responsible for incomplete sulfate recoveries.

The increases in the outgo of calcium and magnesium from the unsupplemented liming materials were considered in connection with absorbed and natural bases, as affecting the persistence of the additions and the protection afforded native materials.

The total losses of calcium and magnesium from the several additions were generally in close agreement, irrespective of the form of the added sulfur, although the periodic outgo was materially influenced by the nature of the sulfur addition.

Each of the six single liming treatments effected a decrease in the outgo of potassium, and no unsupplemented sulfur material produced a positive increase in the outgo of potassium from the acid soil. Each lime and magnesia addition produced a marked decrease in potassium outgo from the several combinations with sulfur materials, the heavier additions being more active in their repressive effect.

Some increase in total nitrate outgo was induced by the single additions of liming materials. Each of the unsupplemented sulfur materials produced a decrease in nitrate outgo, but the lime and magnesia supplements overcame this tendency. The light additions of magnesia caused a greater nitrate outgo than did the light lime supplements. The reverse was true for the heavy additions, in spite of an absolute initial inhibition by the 32-ton calcium oxide supplements.

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THE LAWS OF SOIL COLLOIDAL BEHAVIOR: III. ISOELECTRIC PRECIPITATES[1]

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Soil colloidal materials divide themselves electrokinetically into positive and negative colloids. Most soil colloids consist of silica, humus, and the sesquioxides of iron and aluminum. Silica and humus are strictly electronegative. They adsorb and combine with bases and are, according to the terminology of Michaelis (12), acidoid colloids. The sesquioxides are electrical ampholytes, being electropositive in acid and electronegative in alkaline solutions. The position of their isoelectric point with respect to the pH depends upon the nature of the acid anion which always enters into the composition in their electropositive condition. The sesquioxides adsorb both acids and bases and are therefore ampholytoid colloids.

Since positive and negative sols mutually flocculate and electrically neutralize each other, forming new combinations, the properties of which vary with the relative proportion of each component, it is obviously of the greatest importance to learn something about the laws governing such reactions. In order to understand the soil forming processes it is first necessary to know something about the behavior of the soil colloids, for it is these, which, by flocculation and deposition in one layer and by dispersion and migration to another layer, give rise to the development of soil horizons.

In a previous paper (9) a series of alumino-silicates, isoelectrically precipitated, were studied. In the present work this study has been extended to include other important combinations which can be isoelectrically precipitated. The isoelectric precipitates prepared and studied in this work include: iron and aluminum silicates, humates, phosphates, and hydroxides, together with various mixtures of these combinations.

METHOD

Accurately measured portions of the two solutions, A and B, to be mixed were placed in separate beakers and sufficient water was added to make a combined volume of 50 cc. The mixing was rapidly done by pouring the content of one of the beakers into the other and then back into the first, then again into the second, and finally into a large stoppered pyrex test tube.

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The precipitating zone was found by a preliminary test by running one of the solutions into the other from a burette until a rapid flocculation was observed. This zone was then covered by a series of tubes prepared as explained, either by varying the volume of one of the two solutions or, when the proportions of the solutions were kept constant, by changing the pH by adding HCl or NaOH as the case required. The HCl was always added to the iron and aluminum solutions and the NaOH to the silicate, humate, and phosphate solutions before these solutions were mixed.

The flocculations after the solutions were mixed and after they were allowed to stand over night are recorded in the tables. The latter is represented by crosses, x signifying slight, xx about half complete, xxx nearly complete, and xxxx complete flocculation. The tubes were then shaken and the cataphoresis measurements made as described elsewhere (10). The pH was determined colorimetrically.

From the isoelectric proportions thus found, either directly or by interpolation of the migration velocities, a larger quantity, usually 2.5 liters, was prepared by mixing the same proportions of the various solutions in exactly the same manner. Since the liquid cannot be removed from the floc without disturbing the equilibrium, the composition of the floc was determined by analyzing the supernatant liquid. The Cl and SO_4 ions in the floc were determined by subtracting the quantity found in a measured volume of supernatant liquid from the quantity found in the same volume of liquid which contained the floc.

ISOELECTRIC "HYDROXIDES" OF IRON AND ALUMINUM

The electrokinetic behavior at various degrees of alkalization and the composition of the isoelectric precipitates of the "hydroxides" of aluminum and iron are shown in tables 29–32.

We speak about electropositive iron and aluminum hydroxides, thereby implying that the definite compounds $Fe(OH)_3$ and $Al(OH)_3$ carry a positive charge and migrate to the cathode when, as a matter of fact, these materials are electronegative. It is well known that positive iron and aluminum "hydroxides" contain a certain amount of acid anions. The more acid the medium the greater the quantity of anions in the complex and the more strongly electropositive it is, until the complex resolves itself into a dispersion of single ions. The colloid chemist cannot rightly speak about his colloidal complexes in terms of definite compounds whether he is dealing with negative arsenious sulfide or positive iron hydroxide. A definite compound implies a stoichiometric relationship between the constituent parts. In a colloidal complex there is no such definite relationship, which exists probably only in the interior of the crystal lattice. At the interfaces the free valences attract the various ions present in the solution and these ions combine with the surface layer in proportion as their solution tension and hydration decreases. $BaSO_4$ is positive with an excess of Ba ions and negative with an

TABLE 29

The $AlCl_3$ + NaOH—System No. 3

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 20.0 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B*	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	14.5	Clear	0	.....	...
20	15.0	Instant	xxxx	+1.38	...
20	15.5	Instant	xxxx	+0.61	7.7
20	16.0	Instant	xxxx	±0.0	8.1
20	16.5	Instant	xxxx	−0.47	8.4
20	17.0	Instant	xxxx	−0.67	...
20	17.5	Rapid	xxxx	−1.01	...
20	18.5	Clear	x	.....	...

* Plus water to make 30 cc. or a total volume of 50 cc.

Isoelectric mixture:

5.0 millimols $AlCl_3$ in 1,000 cc.
16.0 millimols NaOH in 1,500 cc.
pH 8.0.

Composition of floc: $(Al_2O_3)_{416} \cdot Al_2O_2Cl_2$ or 0.0048 equivalent Cl per mol Al_2O_3.

TABLE 30

The $FeCl_3$ + NaOH—System No. 4

A. 5.0 millimols $FeCl_3$ in 1,000 cc.
B. 20.0 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	14.5	Clear	0	.....	....
20	14.75	Opal	xxxx	+2.53	6.2
20	14.88	Instant	xxxx	+1.29	6.5
20	15.0	Instant	xxxx	+1.04	6.75
20	15.12	Instant	xxxx	+0.93	6.9
20	15.25	Instant	xxxx	±0.0	7.1
20	15.38	Instant	xxxx	−0.48	7.2
20	15.5	Instant	xxxx	−1.08	7.55
20	15.75	Clear	xxxx	−3.20	8.2

Isoelectric mixture:

5.0 millimols $FeCl_3$ in 1,000 cc.
15.25 millimols NaOH in 1,500 cc.
pH 7.15.

Composition of floc: $(Fe_2O_3)_{387} \cdot Fe_2O_2Cl_2$ or 0.0052 equivalent Cl per mol Fe_2O_3.

TABLE 31

The $Al_2(SO_4)_3$ + NaOH—System No. 2

A. 2.5 millimols $Al_2(SO_4)_3$ in 1,000 cc.
B. 20.0 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	cc.				
20	5.0	Slow	xx	+0.87	...
20	7.5	Rapid	xx	.....	...
20	10.0	Instant	xxxx	+0.87	...
20	14.0	Instant	xxxx	+0.55	...
20	14.5	Instant	xxxx	+0.38	7.3
20	15.0	Instant	xxxx	±0.0	7.6
20	15.5	Instant	xxxx	−0.76	8.0
20	16.5	Instant	xxxx	−1.01	...
20	17.5	Rapid	xxx	.....	...
20	18.5	Slow	xx	−2.33	...

Isoelectric mixture:
2.5 millimols $Al_2(SO_4)_3$ in 1,000 cc.
15.0 millimols NaOH in 1,500 cc.
pH 7.5.
Composition of floc: $(Al_2O_3)_{12.4} \cdot Al_2O_2SO_4$ or 0.0737 mol SO_4 per mol Al_2O_3.

TABLE 32

The $Fe_2(SO_4)_3$ + NaOH—System No. 1

A. 2.5 millimols $Fe_2(SO_4)_3$ in 1,000 cc.
B. 20.0 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	cc.				
20	5.0	Slow	xx	+0.32	...
20	7.5	Rapid	xxx	+0.30	...
20	10.0	Instant	xxxx	+0.30	...
20	14.0	Instant	xxxx	+0.47	...
20	14.5	Instant	xxxx	+0.47	...
20	15.0	Instant	xxxx	+0.61	6.4
20	15.5	Instant	xxxx	+0.40	7.0
20	16.0	Rapid	xxxx	−1.78	7.8
20	16.5	Slow	xxxx	−2.75	...

Isoelectric mixture:
2.5 millimols $Fe_2(SO_4)_3$ in 1,000 cc.
15.59 millimols NaOH in 1,500 cc.
pH 7.05.
Composition of floc: $(Fe_2O_3)_{73} \cdot Fe_2O_2SO_4$ or 0.0135 mol SO_4 per mol Fe_2O_3.

excess of SO_4 ions in the solution (10). AgI is positive with an excess of Ag ions and negative with an excess of I ions in the solution (6). The more highly dispersed these materials are, that is, the greater the surface exposed and the more electropositive or electronegative they are, that is, the greater the excess of a cation or anion in the adsorption layer, the more their composition will depart from a stoichiometric relationship. Hence the "occlusion" spoken of by the analytical chemist.

The composition of a colloidal complex varies constantly with several factors, such as the pH, the composition and concentration of the dispersing solution, and the temperature. Its composition is also influenced by the manner of mixing the reacting solutions, as we shall see. It is also affected by time, as shown by the phenomenom of aging and by a drift in the isoelectric point which is always observed. There must be a balance within the micelle between the positive and negative ions but a stoichiometric relationship between any pair of ions must be accidental.

Returning now to a discussion of the tables, we note, that not even the isoelectric "hydroxides" of iron and aluminum are purely hydroxides. They still retain some of the acid anions. This might be explained as follows: In general all inert substances charge themselves negatively in water. This may be accounted for by assuming the electrical forces within the oriented, interfacial layers of molecules to be such as to attract and fix the OH ions of the water while the H ions (or any other cation which might have displaced the H ions) remain free and diffused into the surrounding water, which then assumes a corresponding positive charge. The resulting complex in the case of negative iron and aluminum hydroxides may be represented thus:

$$Fe(OH)_3OH^- + H^+ \text{ and } Al(OH)_3OH^- + H^+$$

In a NaOH solution these materials, like all others, become strongly electronegative, as the following formula would explain:

$$Fe(OH)_3OH^- + Na^+ \text{ and } Al(OH)_3OH^- + Na^+$$

Both hydroxides adsorb quantities of the base in alkaline solutions. The combination formed is commonly assumed to be in the form of an aluminate, thus:

$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

There is, however, no proof of this. The combination is more likely to be in the form of a simple addition such as $NaAl(OH)_4$. This seems to be the way bases combine with soil colloids (9).

Substances which charge themselves positively in water do so by adsorbing an excess of the cations, thus:

$$(BaSO_4)_x\ Ba^{++} + 2Cl^- \text{ and } (AgI)_x\ Ag^+ + NO_3^-$$

or by dissociating a diffusible anion as the oxychlorides of the sesquioxides, thus:

$$Al_2O_2^{++} + 2Cl^- \text{ or } (Al_2O_3)_x\, Al_2O_2^{++} + 2Cl^-$$

To return to the question, if the iron and aluminum compounds are negative in this form:

$$[Al(OH)_3]_x\, OH^- + Na^+$$

and positive in this:

$$(Al_2O_3)_x\, Al_2O_2^{++} + 2Cl^-$$

then it is evident that the isoelectric complex must still retain some of the acid anions, for otherwise it would be negative.

The isoelectric point is, according to Michaelis (13) that point at which the ampholyte dissociates an equal number of anions and cations. This would of course result in an isoelectric amphoteric complex as represented by the following scheme.

isoelectric complex

− +

diffusible ions

Such an isoelectric ion complex is electrically compensated internally. There is, therefore, nothing to prevent the diffusible ions from diffusing into the surrounding medium, since under these conditions they are always paired. There can, therefore, be no ion atmosphere surrounding an isoelectric particle. This leads to the following important consequences:

The swelling, the viscosity, the osmotic pressure, and the Donnan potential are all at a minimum at the isoelectric point, as found by Loeb in the case of the proteins (5).

The "purification" of a colloid, i.e. the removal of diffusible ions, is most readily accomplished at the isoelectric point.

It is interesting to note that considerably more of the SO_4 ion than of the Cl ion is retained at the isoelectric point. This shows that the SO_4 ion is much less dissociated by the complex than is the monovalent Cl ion. This is in harmony with the observation, reported elsewhere (8), that the amphoteric Aragon soil colloid adsorbed 0.269 milliequivalents SO_4 and only 0.044 m. e. Cl per gram from solutions of the respective acids, but was much more strongly electropositive in the HCl than in the H_2SO_4 solution, the corresponding migration velocities toward the cathode being 0.6 and 2.8μ per second respectively.

TABLE 33

The $AlCl_3$ + Na_2HPO_4—System No. 5

A. 4.96 millimols $AlCl_3$ in 1,000 cc.

B. 10.228 millimols Na_2HPO_4 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	18.0	Opal	xxxx	+1.78	4.0
20	19.0	Slow	xxxx	+0.92	4.3
20	19.5	Rapid	xxxx	.....	...
20	20.0	Rapid	xxxx	−0.15	5.0
20	20.5	Rapid	xxxx	−0.67	5.4
20	21.0	Rapid	xxxx	−0.98	5.7
20	22.0	Slow	xxxx	−1.30	5.95

Isoelectric mixture:

4.96 millimols $AlCl_3$ in 1,000 cc.

10.156 millimols Na_2HPO_4 in 1,500 cc.

pH 4.9.

PO_4 in solution: 5.904 millimols.

PO_4 combined: 4.252 millimols.

Composition: $Al_2O_3 \cdot (P_2O_5)_{0.857}$.

TABLE 34

The $FeCl_3$ + Na_2HPO_4—System No. 6

A. 5.0 millimols $FeCl_3$ in 1,000 cc.

B. 10.228 millimols Na_2HPO_4 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	13.0	Opal	xxxx	+1.68	...
20	15.0	Instant	xxxx	+1.16	3.3
20	17.0	Instant	xxxx	+0.67	3.5
20	18.0	Instant	xxxx	+0.38	3.8
20	18.5	Instant	xxxx	+0.10	4.0
20	19.0	Instant	xxxx	−0.43	4.2
20	19.5	Instant	xxxx	−0.58	4.4
20	21.0	Opal	xxx	−1.68	5.0

Isoelectric mixture:

5.0 millimols $FeCl_3$ in 1,000 cc.

9.512 millimols Na_2HPO_4 in 1,500 cc.

pH 4.0.

PO_4 in solution: 4.943 millimols.

PO_4 combined: 4.569 millimols.

Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.914}$.

TABLE 35

The $AlCl_3$ + Na_3PO_4—System No. 7

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 5.114 millimols Na_3PO_4 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	19.0	Opal	0	.....	...
20	20.0	Opal	xx	.....	...
20	20.5	Slow	xxxx	+1.32	...
20	21.0	Rapid	xxxx	+0.50	5.5
20	21.5	Rapid	xxxx	−0.25	5.7
20	22.0	Rapid	xxxx	−0.70	...
20	22.5	Rapid	xxxx	−1.08	...
20	23.0	Slow	xxxx	−1.10	6.4
20	24.0	Opal	xxxx	.....	...
20	25.0	Opal	xxx	.....	...

Isoelectric mixture:
5.0 millimols $AlCl_3$ in 1,000 cc.
5.482 millimols Na_3PO_4 in 1,500 cc.
pH 5.6.
PO_4 in solution: 1.639 millimols.
PO_4 combined: 3.843 millimols.
Composition: $Al_2O_3 \cdot (P_2O_5)_{0.769}$.

TABLE 36

The $AlCl_3$ + Na_3PO_4 + $NaOH$—System No. 8

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 5.114 millimols Na_2HPO_4 } in 1,000 cc.
20.0 millimols NaOH }

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	9.4	Opal	0	.....	4.6
20	9.5	Opal	0	.....	5.1
20	9.6	Slow	xxxx	+1.38	6.0
20	9.8	Instant	xxxx	−0.38	6.5
20	10.0	Rapid	xxxx	−1.08	6.8
20	10.2	Rapid	xxxx	−1.32	6.9
20	10.4	Slow	xxxx	−1.68	7.0
20	10.5	Opal	xx	.....	7.1

Isoelectric mixture:
5.0 millimols $AlCl_3$ in 1,000 cc.
2.495 millimols Na_2HPO_4 } in 1,500 cc.
9.76 millimols NaOH }
pH 6.45.
PO_4 in solution: 0.085 millimol.
PO_4 combined: 2.410 millimols.
Composition: Al_2O_3 $(P_2O_5)_{0.482}$.

The alumina retains nearly six times as much SO_4 as the iron hydroxide although the alumina is isoelectric at a higher pH. This is in agreement with the observation of analytical chemists that the SO_4 ion is very difficult to remove from the $Al(OH)_3$ precipitate. The OH ion displaces the acid anion more readily in the iron than in the aluminum compound.

The effect of the free divalent sulfate ions is seen in the greatly extended flocculating zone on the positive side. In the case of the sulfates the floc begins to form after the addition of 5 cc. of the alkali solution, whereas the chlorides remain stable up to about 15 cc. of the alkali. This influence is also reflected in the migration velocities. The chloride systems become strongly positive and negative, whereas the sulfate systems attain a high charge only on the negative side.

ISOELECTRIC IRON AND ALUMINUM "PHOSPHATES"

Tables 33–36 show the isoelectric precipitation and the composition of the floc in a series of three "phosphates" of aluminum and one of iron.

In the first place it is evident that the isoelectric "phosphates" are not pure phosphates. Every ion in the system enters to some extent in the combination. Besides the Al (or Fe), the OH, and the PO_4 ions, which together make up the colloidal complex, there is at the isoelectric point some Cl ions and some Na ions. The complex may be represented by the formula

$$NaAl_x\,(OH)_y\,(PO_4)_z\,Cl$$

which by dissociation would yield

$$Na^+ + {}^-[Al_x\,(OH)_y\,(PO_4)]_z{}^+ + Cl^-$$

which would be isoelectric, since the anionic and cationic dissociation balance each other.

This complex is isoelectric at a lower pH than the "hydroxide." The reason for this is that the Cl ions, which persist in the "hydroxide" at a pH above 7.0, are actively displaced by the phosphate ions while the solution is still acid.

The fact that the isoelectric point is displaced far over on the acid side, the displacement being greater with greater PO_4 concentration, shows that the anions HPO_4'' and PO_4''' are, like the OH ions, not appreciably dissociated by the complex. The dissociation of the phosphate ions is not great enough to overcome the effect of the cationic dissociation until we reach a lower pH value. Without the phosphate ions the quantity of Cl in the complex at these pH values would be higher and the complex would, as we have seen, be strongly positive. The phosphate ions, because of their high concentration in the solution, displace the Cl ions in the complex at very much lower pH values than do the OH ions.

The solution tension of the OH ions, that is, the dissociation constant of

the hydroxide, is however, lower than that of the phosphate. In table 36, system no. 8, the pH at the isoelectric point is 6.45, which is equal to a OH ion concentration of 0.282×10^{-7}, whereas the molar phosphate concentration is $0.000085 \div 2.5 = 340.0 \times 10^{-7}$, or over 1,000 times as great, yet the complex formed is over 50 per cent basic. "Normal," or an approach to normal, phosphates of iron and aluminum can therefore only be precipitated in an acid solution with a large excess of phosphate.

As in the case of the "hydroxides" the ferric "phosphate" is isoelectric at a lower pH than the aluminum "phosphate." The ferric "phosphate" contains also a higher phosphate ratio (compare systems 5 and 6) although the phosphate-ion concentration at equilibrium was lower in the ferric system.

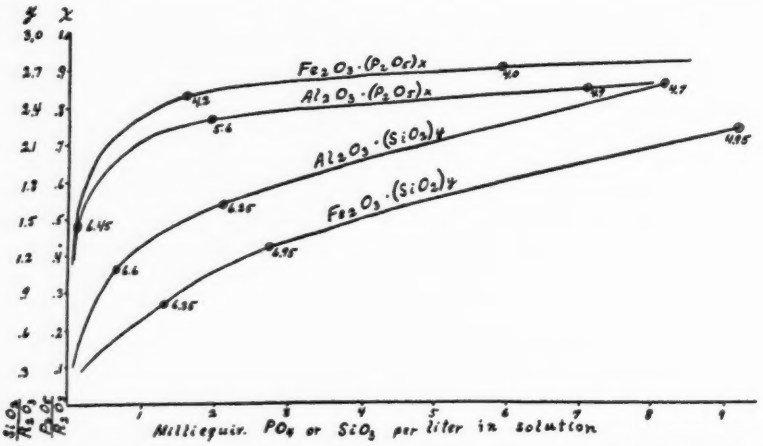


FIG. 6. THE RELATION OF THE PHOSPHATE AND SILICATE CONCENTRATION AND THE pH TO THE COMPOSITION OF THE ISOELECTRIC PRECIPITATES OF ALUMINUM AND FERRIC "PHOSPHATES" AND "SILICATES"

Scattered figures indicate pH

Both the hydroxyl and the phosphate ions are therefore more firmly associated in the ferric than in the aluminum compound. The ferric complex requires, therefore, a lower pH to retain enough Cl ions for the anionic dissociation to balance the cationic dissociation, i.e., the isoelectric condition. It will be noted that the ferric complex does not become as strongly electropositive as the aluminum complex and that the former flocculates on the positive or acid side over a much wider range. The very low positive charge observed in the sulfate-hydroxide systems (1 and 2), and ascribed to the depressing effect of the divalent SO_4 anion, is not found in the phosphate systems. The reason for this is, that on the acid side of the isoelectric point of the latter the monovalent $H_2PO_4^-$ anion predominates.

The results of the experiments with the three aluminum chloride-phosphate mixtures show that each mixture has a different isoelectric point, the pH of which depends on the relative proportions of the two components. The higher the phosphate (the negative component) the lower is the pH at which the system is isoelectric and the greater is the ratio of phosphate to alumina in the precipitate. The higher the proportion of alumina (the positive component) in the mixture, the higher is the isoelectric pH and the lower is the ratio of phosphate to alumina in the precipitate, but the more complete is the removal of the phosphate from solution. In all this the phosphate is identical to the silicate systems previously discussed (9).

The relationship between the PO_4 combined in the isoelectric precipitates and the PO_4 concentration in the solution at equilibrium is shown in figure 6, in which we recognize the familiar "adsorption" curve.

EFFECT OF DILUTION

In order to determine the effect of dilution on the composition of the precipitates, the aluminum "phosphate" mixture no. 5 and the ferric "phosphate" mixture no. 6 were prepared in total volumes of 1 and 10 liters in addition to the isoelectric 2.5-liter systems shown in tables 33 and 34. No cataphoresis measurements were made but the precipitation was complete in all cases.

Mixture No. 5 (concentrated)
4.96 millimols $AlCl_3$ in 500 cc.
10.156 millimols Na_2HPO_4 in 500 cc.
pH 4.85
PO_4 in solution: 5.670 millimols
PO_4 combined: 4.486 millimols
Composition: $Al_2O_3 \cdot (P_2O_5)_{0.897}$

Mixture No. 5 (diluted)
4.96 millimols $AlCl_3$ in 5,000 cc.
10.156 millimols Na_2HPO_4 in 5,000 cc.
pH 5.2
PO_4 in solution: 6.205 millimols
PO_4 combined: 3.951 millimols
Composition: $Al_2O_3 \cdot (P_2O_5)_{0.790}$

Mixture No. 6 (concentrated)
5.0 millimols $FeCl_3$ in 500 cc.
9.512 millimols Na_2HPO_4 in 500 cc.
pH 3.7
PO_4 in solution: 4.656 millimols
PO_4 combined: 4.856 millimols
Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.971}$

Mixture No. 6 (diluted)
5.0 millimols $FeCl_3$ in 5,000 cc.
9.512 millimols Na_2HPO_4 in 5,000 cc.
pH 4.2
PO_4 in solution: 5.343 millimols
PO_4 combined: 4.169 millimols
Composition: $(Fe_2O_3) \cdot (P_2O_5)_{0.834}$

An increase in concentration lowered the pH whereas a decrease in concentration had the opposite effect. In spite of this variation in the pH it will be seen that, if we reduce the millimols PO_4 in the solution to milliequivalents per liter and plot this value with the composition ratio as in figure 6, the points in the case of the aluminum compound will lie very nearly on the curve. The ferric "phosphate" composition ratios are higher in each case, as shown by the greater steepness of this curve.

THE COMPOSITION OF POSITIVE AND NEGATIVE FERRIC "PHOSPHATE"

The composition of the strongly negative and of the strongly positive precipitates was compared with the composition of the isoelectric precipitate

in systems containing the same proportions of the major reacting materials. Ferric "phosphate" was found to be admirably suited for this experiment because of the variations in color with the degree of saturation. The normal ferric phosphate is pale greenish gray but becomes yellowish and finally brownish as the compound becomes more basic.

By adding NaOH or HCl to the isoelectric mixture no. 6 (table 34) the system was made strongly negative or positive. The colloid, however, became more or less stable, and as a result the flocculation had to be forced by adding 500 millimols NH_4Cl. The mixtures were as follows:

Electropositive mixture No. 6a

5.0 millimols $FeCl_3$ + 2.5 millimols HCl in 1,000 cc.
9.512 millimols Na_2HPO_4 + 500 millimols NH_4Cl in 1,500 cc.
pH 3.2
PO_4 in solution: 4.589
PO_4 combined: 4.923
Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.985}$
Color: pale greenish gray
NH_4 adsorbed: 0.48 milliequivalents

Isoelectric mixture No. 6

As given in table 34
Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.914}$
Color: pale yellowish, greenish gray

Electronegative mixture No. 6b

5.0 millimols $FeCl_3$ in 1,000 cc.
9.512 millimols Na_2HPO_4 + 5.0 millimols NaOH + 500 millimols NH_4Cl in 1,500 cc.
pH 6.5
PO_4 in solution: 4.813 millimols
PO_4 combined: 4.699 millimols
Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.940}$
Color: yellowish
NH_4 adsorbed: 2.01 milliequivalents

Electronegative mixture No. 6bb

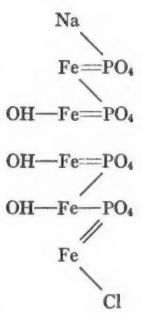
5.0 millimols $FeCl_3$ in 1,000 cc.
9.512 millimols Na_2HPO_4 + 10.0 millimols NaOH + 500 millimols NH_4Cl in 1,500 cc.
pH 7.1
PO_4 in solution: 4.894 millimols
PO_4 combined: 4.618 millimols
Composition: $Fe_2O_3 \cdot (P_2O_5)_{0.924}$
Color: brownish
NH_4 adsorbed: 2.00 milliequivalents

The ratio of P_2O_5 to Fe_2O_3 has increased from 0.914 in the isoelectric complex to 0.985 in the positive complex. This would be expected because the positive complex was formed in a more acid solution in which OH-ion concentration was very low. The OH ions offered, therefore, very little competition, resulting in a less basic complex. This was also indicated by the color, which

was a trace lighter in the positive floc. In the case of the negative complex we meet with an anomali. We would anticipate this complex to be more basic in composition, as is indeed indicated by the color, which shifts to yellow and then to brown as the OH-ion concentration is increased. But the analysis reveals an increase in the composition ratio to 0.940 at a pH of 6.5 and a smaller increase to 0.924 at a pH of 7.1.

The color changes show that in the negative complexes the iron must be in actual combination with less PO_4 than in the isoelectric complex, yet the analysis shows a higher proportion in the negative complexes. We are here dealing with a colloidal complex formation which, under the conditions of the experiment, is comparatively simple. In the soil, where there is a multitude of different ions, the complex would be complicated indeed. But even here, if we are to explain what is taking place it will be necessary to free ourselves of the dogma of stoichiometry and definite proportions.

If the ferric phosphate hydrolyzes, that is, if the OH ions displace the PO_4 ions as the pH is increased, then the actual number of linkages between Fe and PO_4 is reduced but that does not necessarily mean that the complex will be poorer in PO_4 ions. In order to provide us with something tangible as a basis for our line of reasoning let the following greatly abbreviated formula represent the isoelectric complex:



This complex would have the composition

$$Fe_2O_3(P_2O_5)_{0.80}$$

If we now represent the electronegative complex by the following formula:

$$OH—Fe{=}PO_4—NH_4$$

$$OH—Fe{=}PO_4—Na$$

$$OH—Fe{=}PO_4—H$$

$$OH—Fe{=}PO_4—NH_4$$

$$OH—Fe{=}PO_4—H$$

we get a combination with the following apparent composition

$$Fe_2O_3(P_2O_5)_{1.0}$$

as if it were a normal phosphate, although this complex is in reality more basic, as far as the ferric component is concerned, than the previous one, in which the PO_4 content is lower.

If the OH ions have displaced some of the PO_4 valences then the latter must be satisfied by linking themselves with a corresponding number of cations in the solution. This was tested by a determination of the quantity of NH_4 ions which were removed from solution. It was found that whereas the electropositive precipitate adsorbed only 0.48 milliequivalents the two electronegative precipitates adsorbed 2.01 and 2.00 milliequivalents NH_4.

This structure of the complex will explain the mechanism of ion adsorption and exchange which these phosphates possess in common with the silicates and other substances. Since this subject will be discussed further in a paper on ion adsorption and exchange we will now turn our attention to another series of isoelectric precipitates.

ISOELECTRIC "SILICATES"

Tables 37–39 show the isoelectric precipitation and the composition of the floc of aluminum and iron "silicates."

The silicate ion, like the phosphate, displaces the isoelectric point to the acid side, the displacement increasing in direct proportion to the silicate concentration in the solution and the proportion of silica which has entered into combination with the complex. The silicate ions must therefore displace the easily dissociating Cl ions. This suppresses the anionic dissociation and at the same time increases the cationic dissociation because the silicated, like the phosphated, complex adsorbs cations from the solution. For the two forms of dissociation to be equalized (the isoelectric condition) the pH must necessarily be lowered. The higher the silicate content of the complex the lower the pH at which a sufficient number of Cl ions are retained for the isoelectric condition.

The quantity of Cl ions carried down in the floc was determined in a number of the "silicate" systems. The quantities varied between 0.030 and 0.007 milliequivalent Cl per millimol Al_2O_3 or Fe_2O_3. The rather wide variation is probably chiefly due to errors. The results show, nevertheless, that a small quantity of Cl (or any other dissociating and readily diffusible anion) is essential for the isoelectric as well as for the electropositive condition.

Since, at a given concentration and pH, less of the SiO_3 than of the PO_4 combines with the complex it is evident that the SiO_3 competes less strongly with the OH ions. This is to be ascribed to the low dissociation constant of silicic acid and possibly also to a lower solubility of the phosphate than of the silicate. The relationship is brought out more clearly in figure 6. It will be

TABLE 37A

The $AlCl_3 + Na_2SiO_3 + HCl$—System No. 9

A. 5.0 millimols $AlCl_3$ + 22.5 millimols HCl in 1,000 cc.
B. 15.0 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	21.0	Opal	xxxx	+1.12	4.35
20	21.2	Slow	xxxx	+1.08	4.35
20	21.5	Instant	xxxx	+0.82	4.4
20	22.0	Instant	xxxx	+0.40	4.5
20	22.5	Instant	xxxx	−0.76	5.0
20	23.0	Instant	xxxx	−1.44	5.65
20	24.0	Instant	xx	.....	6.1
20	25.0	Opal	0	.....	....

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 6.66$.

5.0 millimols $AlCl_3$ + 22.5 millimols HCl in 1,000 cc.
16.65 millimols Na_2SiO_3 in 1,500 cc.
pH 4.7.
SiO_2 in solution: 10.207 millimols.
Al_2O_3 in solution: 0.039 millimols.
Composition of floc: $Al_2O_3\ (SiO_2)_{2.26}$.

TABLE 37B

The $FeCl_3 + Na_2SiO_3 + HCl$—System No. 10

A. 5.0 millimols $FeCl_3$ + 22.5 millimols HCl in 1,000 cc.
B. 15.0 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	21.5	Opal	0	.....	...
20	22.5	Opal	xxx	+0.84	4.2
20	23.0	Instant	xxxx	−0.80	5.3
20	23.5	Instant	xxxx	−1.68	6.1
20	24.0	Rapid	xxx	−1.78	6.4
20	24.5	Opal	x	.....	...

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 6.82$.

5.0 millimols $FeCl_3$ + 22.5 millimols HCl in 1,000 cc.
17.06 millimols Na_2SiO_3 in 1,500 cc.
pH 4.95.
SiO_2 in solution: 11.481 millimols.
Fe_2O_3 in solution: 0.025 millimols.
Composition of floc: $Fe_2O_3\ (SiO_2)_{2.26}$.

TABLE 38A

The $AlCl_3 + Na_2SiO_3$—System No. 11

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 7.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM	pH
		After mixing	Overnight		
cc.	*cc.*				
20	17.4	Opal	0	.....	...
20	17.6	Slow	xxxx	+1.38	5.7
20	17.8	Instant	xxxx	+0.76	6.1
20	18.0	Instant	xxxx	−0.67	6.4
20	18.5	Slow	xx	.....	...

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 2.68$.

5.0 millimols $AlCl_3$ in 1,000 cc.
6.713 millimols Na_2SiO_3 in 1,500 cc.
pH 6.25.
SiO_2 in solution: 2.641 millimols.
Al_2O_3 in solution: 0.005 millimols
Composition of floc: $Al_2O_3\ (SiO_2)_{1.62}$.

TABLE 38B

The $FeCl_3 + Na_2SiO_3$—System No. 12

A. 5.0 millimols $FeCl_3$ in 1,000 cc.
B. 7.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	17.4	Opal	0	.....	....
20	17.6	Slow	xxx	+0.65	5.65
20	17.8	Instant	xxxx	−0.34	6.1
20	18.0	Instant	xxxx	−1.38	6.3
20	18.5	Rapid	xxx	−1.59	6.6

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 2.66$.

5.0 millimols $FeCl_3$ in 1,000 cc.
6.65 millimols Na_2SiO_3 in 1,500 cc.
pH 5.95.
SiO_2 in solution: 3.452 millimols
Fe_2O_3 in solution: 0.0125 millimols.
Composition of floc: $Fe_2O_3(SiO_2)_{1.29}$.

TABLE 39A

The $AlCl_3 + Na_2SiO_3 + NaOH$—System No. 13

A. 5.0 millimols $AlCl_3$ in 1,000 cc.
B. 7.5 millimols Na_2SiO_3 + 15 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	9.1	Opal	0	.....	....
20	9.2	Slow	x	.....	....
20	9.3	Instant	xxxx	+1.38	6.35
20	9.4	Instant	xxxx	+0.87	6.55
20	9.5	Instant	xxxx	− slight	6.7
20	10.0	Opal	0	.....	....

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 1.43$.

5.0 millimols $AlCl_3$ in 1,000 cc.
3.562 millimols Na_2SiO_3 + 7.124 millimols NaOH in 1,500 cc.
pH 6.6.
SiO_2 in solution: 0.828 millimols.
Al_2O_3 in solution: trace.
Composition of floc: $Al_2O_3(SiO_2)_{1.09}$.

TABLE 39B

The $FeCl_3 + Na_2SiO_3 + NaOH$—System No. 14

A. 5.0 millimols $FeCl_3$ in 1,000 cc.
B. 7.5 millimols Na_2SiO_3 + 15 millimols NaOH in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	9.3	Opal	0	.....	....
20	9.4	Instant	xxxx	+1.26	5.7
20	9.5	Instant	xxxx	+0.94	6.0
20	9.6	Instant	xxxx	−0.36	6.45
20	9.8	Instant	xxxx	−1.59	6.65
20	10.0	Opal	0	.....	....

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 1.44$.

5.0 millimols $FeCl_3$ in 1,000 cc.
3.588 millimols Na_2SiO_3 + 7.176 millimols NaOH in 1,500 cc.
pH 6.35.
SiO_2 in solution: 1.631 millimols.
Fe_2O_3 in solution: trace.
Composition of floc: $Fe_2O_3(SiO_2)_{0.79}$.

seen that the position of the two pairs of curves is reversed. The ferric phosphate curve is steeper than that of aluminum and the aluminum silicate curve is steeper than that of the iron. Since $Fe(OH)_3$ is more insoluble than $Al(OH)_3$, as shown by the fact that ferric salts are more easily hydrolyzed, it follows from the position of the curves that ferric phosphate is more insoluble than aluminum phosphate. It does not necessarily follow, however, that aluminum silicate is more insoluble than ferric silicate, because the firmer union between Fe and OH would alone result in a lower silicate content. Ferric silicate is therefore more readily hydrolyzed than is aluminum silicate. This is quite evident in the natural soil colloids (16) and explains the formation of ferruginous clays.

As in the case of the "hydroxide" and "phosphate," the "silicate" of iron is isoelectric at a lower pH than the corresponding aluminum compound. In the case of the more highly silicated complexes which are isoelectric at low pH values (between 4.0 and 5.0) this relationship reversed itself, the aluminum complex being isoelectric at the lowest pH.

The preceding isoelectric "silicate" complexes may be represented by the following general formula

$$Na^+ -[Al_x (OH)_y (SiO_3)_z]^+ Cl^-.$$

This does not mean that the Na ions must equal the Cl ions. It is only the dissociated diffusible cations and anions which must be equal at the isoelectric point. The degree of dissociation may be very different. Also, the preceding formula takes no account of the H ions which are also present in the system and which must, to a large extent, displace the Na ions.

The aforementioned complex may be termed the "chloridated complex" as distinguished from another very illuminating example—the sulfated, silicate complex.

THE SULFATED, SILICATE COMPLEX

In tables 40a and 40b the same concentrations as in tables 38a and 38b were used but instead of the chlorides of iron and aluminum, the sulfates were employed.

A comparison of the composition of the "sulfated silicates" with the corresponding "chloridated silicates" in tables 38a and 38b shows that the sulfated complex is isoelectric with a lower silica content, with a considerably higher proportion of SO_4 than the proportion of Cl in the chloridated complex, and at a lower pH value. This is all in harmony with the preceding observations that the SO_4 ion is more firmly associated in the complex. Since the SO_4 ions are less dissociated than the Cl ion, a greater proportion must be present in order that the anionic dissociation shall balance the cationic dissociation at the isoelectric point. As in the case of the "hydroxide," the isoelectric pH is lower in the sulfated complex.

By displacing a highly dissociating anion like the Cl ion by a less dissociat-

TABLE 40A

The $Al_2(SO_4)_3$ + Na_2SiO_3—System No. 15

A. 2.5 millimols $Al_2(SO_4)_3$ in 1,000 cc.

B. 7.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	8	Slow	xxxx	+1.01	4.1
20	10	Rapid	xxxx	.....	4.2
20	12	Instant	xxxx	+0.68	4.3
20	14	Instant	xxxx	+0.67	4.45
20	16	Instant	xxxx	+0.50	5.1
20	17	Instant	xxxx	+0.42	5.75
20	18	Instant	xxxx	−0.95	6.4
20	19	Opal	x	.....	....

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 2.60$.

2.5 millimols $Al_2(SO_4)_3$ in 1,000 cc.

6.488 millimols Na_2SiO_3 in 1,500 cc.

pH 6.1.

SiO_2 in solution: 3.866 millimols.

SO_4 in solution: 7.153 millimols.

Al_2O_3 in solution: None.

SO_4 added: 7.500 millimols.

Composition of floc: $Al_2O_3(SiO_2)_{1.05}(SO_3)_{0.139}$ or $Al_2(OH)_{3.622}(SiO_3)_{1.05}(SO_4)_{0.139}$.

TABLE 40B

The $Fe_2(SO_4)_3$ + Na_2SiO_3—System No. 16

A. 2.562 millimols $Fe_2(SO_4)_3$ in 1,000 cc.

B. 7.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.	*cc.*				
20	10	Slow	xxx	+0.45	....
20	12	Rapid	xxxx	+0.36	....
20	14	Instant	xxxx	+0.28	3.4
20	16	Instant	xxxx	+0.33	4.0
20	17	Instant	xxxx	+0.32	4.8
20	18	Instant	xxxx	−0.44	5.75
20	19	Instant	xxx	−2.20	6.5
20	20	Opal	0	.....	....

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 2.54$.

2.562 millimols $Fe_2(SO_4)_3$ in 1,000 cc.

6.525 millimols Na_2SiO_3 in 1,500 cc.

pH 5.4.

SiO_2 in solution: 4.694 millimols.

SO_4 in solution: 7.247 millimols.

Fe_2O_3 in solution: None.

SO_4 added: 7.687 millimols.

Composition of floc: $Fe_2O_3(SiO)_{0.716}(SO_3)_{0.176}$ or $Fe_2(OH)_{4.218}(SiO_3)_{0.716}(SO_4)_{0.176}$.

ing anion, the isoelectric pH is always displaced in the direction of greater acidity. [Conversely if we displace highly dissociating cations by slightly dissociating cations we will displace the isoelectric pH in the opposite direction. Thus, if we add aluminum or ferric chloride to an isoelectric silicate or phosphate, the system will be electropositive at the same pH, the isoelectric pH being now higher. This fact is of great importance in relation to ion adsorption and exchange. Soil colloids high in aluminum and iron possess a low cation exchange capacity, the Al and Fe not themselves being exchangeable, and these colloids are isoelectric within the usual range of soil reactions (8)].

It is evident that the SiO_3 ion does not displace the more firmly associated SO_4 as readily as it displaces the Cl ion. Although the silicate concentration in the solution at equilibrium is higher and the pH is lower in the sulfate than in the corresponding chloride systems, the number of mols of SiO_2 per mol sesquioxide has decreased from 1.63 in the chloridated to 1.05 in the sulfated aluminum silicate and from 1.29 to 0.715 in the corresponding ferric compounds. But the decrease in the silicate content is only partly accounted for by the SO_4 content. The sulfated silicate complexes are more basic than the corresponding chloridated complexes, indicating a firmer hydroxide union in the former.

At the lower pH values at which the "silicates" are isoelectric, more SO_4 remains in the complex than was found in the isoelectric "hydroxides." This would indicate that the silicate complex contains a higher proportion of dissociating (exchangeable) cations than the hydroxide complex. (This we know to be the case.) A larger proportion of SO_4 ions is therefore necessary in order that the anionic dissociation shall balance the cationic dissociation.

In the absence of silicate, how much SO_4 would be found in the complexes at the same pH values? To answer this question the same number of millimols of $Al_2(SO_4)_3$ and $Fe_2(SO_4)_3$ were alkalized with NaOH to the same pH values, i.e., 6.1 and 5.4 respectively, and the supernatant liquids analyzed for SO_4. This procedure is made possible by the fact that in the presence of the divalent SO_4 anion the positive sol is flocculated completely over a wide range as is shown in the tables. The results were as follows:

2.5 millimols $Al_2(SO_4)_3$ in 2,500 cc.	2.562 millimols $Fe_2(SO_4)_3$ in 2,500 cc.
pH 6.1 adjusted with NaOH	pH 5.4 adjusted by NaOH
SO_4 in system: 7.500 millimols	SO_4 in system: 7.687 millimols
SO_4 in solution: 6.380 millimols	SO_4 in solution: 6.977 millimols
Composition of floc: $Al_2O_3(SO_3)_{0.448}$ or $Al_2(OH)_{5.104}(SO_4)_{0.448}$	Composition of floc: $Fe_2O_3(SO_3)_{0.277}$ or $Fe_2(OH)_{5.446}(SO_4)_{0.277}$

In the absence of the silicate and at the same pH, the complexes have a higher SO_4 content and are electropositive. In the isoelectric complexes, portions of both of the OH and SO_4 ions have been displaced by the SiO_3 ions.

All the ions in the system mutually displace one another in the colloidal

complex and thus affect the composition and behavior of the complex. The displacing power or association constant of the ions in the systems thus far considered seems to be

$$OH > PO_4 > SiO_3 > SO_4 > Cl$$

But the association constant apparently varies with the composition of the colloidal ion complex, which is quite natural. Since the composition of the complex varies with the nature and concentration of each ion in the solution, no fixed magnitude can be assigned to the displacing power of any ion. This will explain the many discrepancies in the various ion series suggested by different investigators.

The law governing ion exchange may be stated thus: All ions in the solution displace one another in the complex in proportion to the product of their concentration (activity) and the association constant.

EFFECT OF DILUTION ON THE PH AND COMPOSITION OF ISOELECTRIC "SILICATES"

To study the effect of dilution a mixture ratio of $\frac{SiO_2}{R_2O_3} = 10.0$ was maintained in each case. The systems were rendered isoelectric by adjusting the pH by small increments of HCl which was added to the aluminum or ferric chloride before these solutions were mixed with the silicate. Tables 41a and 41b represent the dilute and tables 42a and 42b represent the concentrated systems, the silica/sesquioxide ratio being 10 in each case.

The results are similar to those of the dilution experiments with the phosphate and fit the curves in figure 6 fairly well. The lower the dilution the greater is the number of silicate ions entering into combination with the complex. In the concentrated systems the isoelectric pH is markedly displaced to the more acid side. The highly dissociating Cl ions are here so much more energetically displaced by the higher SiO_3-ion concentration that a lower pH is necessary to leave a sufficient residue of Cl ion in the complex to balance the cationic dissociation and render the colloid isoelectric. There are, therefore, two factors which, in the more concentrated isoelectric system, lead to a more highly silicated floc. In the first place the silicate-ion concentration is higher, and in the second place the OH-ion concentration is lower; consequently these ions compete less for a place in the complex.

As already has been noted, the isoelectric pH is lower in the aluminum than in the ferric silicate system at low pH values. At higher pH values the order is reversed.

It is significant that even though the equilibrium silicate concentration attains considerable proportions in the concentrated system, the ratio of silica to sesquioxide in the floc approaches, but does not exceed, a value of 3.0, which would be that of the normal silicate. This indicates that the reaction is between single ions, for if it were a combination between colloidal aggregates of sesquioxide and silica as in the mutual flocculation of positive and

TABLE 41A

The dilute $AlCl_3 + Na_2SiO_3$—System No. 25

A. 2.0 millimols $AlCl_3$ in 1,000 cc.
B. 10.0 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 cc. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM	pH
		After mixing	Overnight		
	cc.				
0.3000	20	Opal	0	.....	...
0.3050	20	Instant	xxxx	−1.44	...
0.3075	20	Rapid	xxxx	−0.55	5.6
0.3100	20	Slow	xxxx	+0.61	5.0
0.3200	20	Opal	0	.....	...

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 10.0$.

2.0 millimols $AlCl_3$ + 15.43 millimols HCl in 1,000 cc.
10.0 millimols Na_2SiO_3 in 1,500 cc.
pH 5.6.
SiO_2 in solution: 7.872 millimols.
Al_2O_3 in solution: 0.016 millimols.
Composition of floc: $Al_2O_3(SiO_2)_{2.15}$.

TABLE 41B

The dilute $FeCl_3 + Na_2SiO_3$—System No. 26

A. 2.0 millimols $FeCl_3$ in 1,000 cc.
B. 10.0 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 cc. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
	cc.				
0.2950	20	Clear	0	.....	...
0.3000	20	Rapid	xxx	−1.89	...
0.3050	20	Instant	xxxx	−1.05	...
0.3075	20	Rapid	xxxx	−0.65	5.6
0.3100	20	Opal	xxxx	+0.50	4.4
0.3200	20	Opal	0	.....	...

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 10.0$.

2.0 millimols $FeCl_3$ + 15.44 millimols HCl in 1,000 cc.
10.0 millimols Na_2SiO_3 in 1,500 cc.
pH 5.4.
SiO_2 in solution: 8.170 millimols.
Fe_2O_3 in solution: 0.010 millimols.
Composition of floc: $Fe_2O_3(SiO_2)_{1.16}$.

TABLE 42A

The concentrated $AlCl_4$ + Na_2SiO_3—System No. 27

A. 7.5 millimols $AlCl_3$ in 1,000 cc.

B. 37.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 CC. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
	cc.				
1.14	20	Slow	x	.....	....
1.15	20	Instant	xxx	−1.51	4.6
1.16	20	Instant	xxxx	−1.04	....
1.17	20	Instant	xxxx	−0.74	....
1.18	20	Instant	xxxx	−0.25	4.3
1.19	20	Instant	xxxx	±0.0	4.25
1.20	20	Instant	xxxx	+0.43	4.2
1.22	20	Instant	xxxx	+1.09	....
1.26	20	Slow	xx	+1.12	4.1

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 10.0$.

7.5 millimols $AlCl_3$ + 59.5 millimols HCl in 1,000 cc.

37.5 millimols Na_2SiO_3 in 1,500 cc.

pH 4.2.

SiO_2 in solution: 26.840 millimols.

Al_2O_3 in solution: 0.076 millimols.

Composition of floc: $Al_2O_3(SiO_2)_{2.90}$.

TABLE 42B

The concentrated $FeCl_3$ + Na_2SiO_3—System No. 28

A. 7.5 millimols $FeCl_3$ in 1,000 cc.

B. 37.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 CC. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
	cc.				
1.13	20	Opal	0	.....	...
1.14	20	Instant	xxx	−1.70	...
1.15	20	Instant	xxxx	−1.36	5.0
1.16	20	Instant	xxxx	±0.0	4.2
1.17	20	Rapid	xx	+0.61	...
1.18	20	Opal	0	.....	...

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 10.0$.

7.5 millimols $FeCl_3$ + 58.0 millimols HCl in 1,000 cc.

37.5 millimols Na_2SiO_3 in 1,500 cc.

pH 4.35.

SiO_2 in solution: 26.593 millimols.

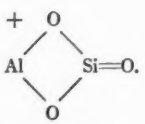
Fe_2O_3 in solution: 0.042 millimols.

Composition of floc: $Fe_2O_3\ (SiO_2)_{2.94}$.

negative sols, where only the surface layer of molecules are able to react, we could hardly expect such regularity in the composition ratio.

In the higher concentrations the silica shows by itself a tendency to flocculate when sodium silicate is slightly acidified. There is, therefore, the possibility in systems of low dilution of flocculating free silica together with the isoelectric complex. This might have happened in the concentrated ferric system in which the composition ratio of the floc was extraordinarily high. Such complications, which are of course not met with in the phosphate systems, are always present in the "humate" systems as we shall see later, for "humuc acid" is still more colloidal than silica.

It will be noted that Fe and, to a higher degree, Al appear in the solution in increasing quantities with a lowering of the pH, but it is doubtful whether they dissociate as free metal cations. The author has established the fact that when orthoclase is electrodialyzed, aluminum appears *together with silica* in the cathode chamber after the pH of the feldspar has been reduced to a certain value by the removal of potassium. It was then suggested that the aluminum and silica exist in acid solution in the form of a complex cation as exemplified by the following formula (9)



The structure of this ion is identical with the structure assumed for the electropositive colloidal silicate complex and is arrived at by the further assumption that the latter is capable of splitting off single such ions or ion aggregates small enough to pass through the membrane. In other words, the positive silicate complex is slightly soluble and the aluminum and iron found in the acid soil solution are not entirely due to a breaking up of the complex. It would be interesting to determine whether the negative complex similarly yields a diffusible aluminum silicate anion when saturated with the strongly dissociating Na ions.

Odén (14) and later Wiegner and Palmann (19) observed silica migrating to the cathode when a soil is electrodialyzed. This fact was originally overlooked by the author but was predicted in connection with the feldspar experiment and has since been verified. That the aforementioned isoelectric precipitates yield a cathodic complex containing silica and sesquioxides will be shown later.

INFLUENCE OF STATE OF DISPERSION OF REACTING MATERIALS ON COMPOSITION OF PRECIPITATES

In the following experiments a mixture ratio of 14 mols silica to 1 mol sesquioxide was maintained throughout. The HCl was added, as before,

TABLE 43A

The ($AlCl_3$ + HCl) + Na_2SiO_3—System No. 29

A. 2.5 millimols $AlCl_3$ in 1,000 cc.
B. 17.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 CC. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
	cc.				
0.580	20	Clear	0	.....	...
0.590	20	Opal	0	.....	...
0.595	20	Rapid	xx	−1.97	5.5
0.600	20	Instant	xxxx	−1.31	5.0
0.605	20	Rapid	xxxx	+0.20	4.6
0.610	20	Slow	xxxx	+0.67	4.4
0.620	20	Opal	xx	+0.82	4.25

Isoelectric mixture: $\frac{SiO_2}{Al_2O_3} = 14.0$.

2.5 millimols $AlCl_3$ + 30.2 millimols HCl in 1,000 cc.
17.5 millimols Na_2SiO_3 in 1,500 cc.
pH 4.7.
SiO_2 in solution: 14.138 millimols.
Al_2O_3 in solution: 0.052 millimols.
Composition of floc: $Al_2O_3(SiO_2)_{2.80}$.

TABLE 43B

The ($FeCl_3$ + HCl) + Na_2SiO_3—System No. 30

A. 2.5 millimols $FeCl_3$ in 1,000 cc.
B. 17.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A 20 CC. + HCl MILLIMOLS	SOLUTION B	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
	cc.				
0.590	20	Opal	xx	−1.78	...
0.595	20	Instant	xxx	−1.44	5.8
0.600	20	Opal	xxxx	−0.95	5.0
0.6025	20	Opal	xxxx	+0.28	4.4
0.605	20	Opal	0	.....	...
0.608	20	Clear	0	.....	...

Isoelectric mixture: $\frac{SiO_2}{Fe_2O_3} = 14.0$.

2.5 millimols $FeCl_3$ + 30.09 millimols HCl in 1,000 cc.
17.5 millimols Na_2SiO_3 in 1,500 cc.
pH 4.7.
SiO_2 in solution: 14.619 millimols.
Fe_2O_3 in solution: 0.032 millimols.
Composition of floc: $Fe_2O_3(SiO_2)_{2.36}$.

TABLE 44A

The $AlCl_3$ + (Na_2SiO_3 + HCl)—System No. 31

A. 2.5 millimols $AlCl_3$ in 1,000 cc.

B. 17.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B 20 CC. + HCl MILLIMOLS	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.					
20	0.610	Clear	0	.....	4.3
20	0.615	Opal	xxxx	−1.01	4.25
20	0.620	Slow	xxxx	−0.87	4.15
20	0.630	Opal	xxxx	−0.80	4.10
20	0.640	Clear	xxxx	.....	4.05
20	0.650	Clear	xxxx	−0.76	3.9

Electronegative mixture: $\frac{SiO_2}{Al_2O_3} = 14.0$.

2.5 millimols $AlCl_3$ in 1,000 cc.

17.5 millimols Na_2SiO_3 + 31.0 millimols HCl in 1,500 cc.

pH 4.15.

SiO_2 in solution: 5.637 millimols.

Al_2O_3 in solution: 0.105 millimols.

Composition of floc: $Al_2O_3(SiO_2)_{10.35}$.

TABLE 44B

The $FeCl_3$ + (Na_2SiO_3 + HCl)—System No. 32

A. 2.5 millimols $FeCl_3$ in 1,000 cc.

B. 17.5 millimols Na_2SiO_3 in 1,000 cc.

SOLUTION A	SOLUTION B 20 CC. + HCl MILLIMOLS	FLOCCULATION		μ/SEC. 1 VOLT/CM.	pH
		After mixing	Overnight		
cc.					
20	0.595	Clear	0	.....	...
20	0.5975	Clear	0	.....	...
20	0.600	Opal	0	.....	...
20	0.6025	Clear	xxxx	−0.25	4.2
20	0.605	Clear	0	.....	...
20	0.615	Clear	0	.....	...

Electronegative mixture: $\frac{SiO_2}{Fe_2O_3} = 14.0$.

2.5 millimols Fe_2Cl_3 in 1,000 cc.

17.5 millimols Na_2SiO_3 + 30.125 millimols HCl in 1,500 cc.

pH 4.2.

SiO_2 in solution: 7.235 millimols.

Fe_2O_3 in solution: 0.054 millimols.

Composition of floc: $Fe_2O_3(SiO_2)_{8.59}$.

in small increments, sufficient to cover the whole range of precipitation. The acid was added to the $AlCl_3$ and $FeCl_3$ solutions in one set, and to the silicate solution, before mixing, in the second set. This resulted in partly changing the silica to the colloidal condition before it reacted with the Al and Fe. The results are shown in tables 43a and 43b and in 44a and 44b.

In the two experiments where the HCl was added to the chloride solutions before mixing, the composition of the floc is in line with all previous experiments. The points representing the composition ratio and the silicate concentration at equilibrium come in close proximity of the silicate curves in figure 6. It would seem, therefore, that no matter how high the ratio of silica to sesquioxide is in the mixture, an isoelectric floc will form, in which the composition ratio is smaller than 3.0, provided the system is kept sufficiently dilute. In the author's previous experiments (9) the composition ratio already exceeded this value at a mixture ratio of 8.0 but the system, it will be noted, was then more concentrated. There is evidently a critical point at which free silica flocculates together with the complex. The floc has then no isoelectric point but remains negative and in systems of still higher concentration the flocculation becomes incomplete.

The conditions are then similar to those in the last two experiments where the HCl was added to the silicate before this solution was mixed with the chlorides. The acid changes the silica partly to the colloidal condition. Where, under the conditions of true solution, single ions combined, there is now a combination of Al and Fe ions with aggregates of silicate molecules and ions. The ratio of silica to sesquioxides in the resulting complex must therefore be abnormally high. Since the "free" silica in the complex combines with the various diffusible cations in the solution (in this case Na and H) the cationic dissociation will be increased. The complex will therefore be more electronegative and may have no isoelectric point, for although it contains a certain number of diffusible anions (in this case Cl ions) at low pH values, the anionic dissociation may never balance that of the cations.

It will be noted in the tables 44a and 44b that a reduction in the dispersion of the silicate resulted in a floc in which the ratio of silica to sesquioxide is enormously increased and also that the complex remains negative over the entire range of flocculation. The ferric complex shows a very narrow zone of flocculation. This is important, for it shows that silica exerts a protective action on the iron, as definitely shown by the work of Reifenberg (15). In general, ferric "silicates" show a more narrow zone of flocculation than the aluminum "silicates."

INFLUENCE OF DIVALENT CATIONS ON THE ALUMINUM AND FERRIC "SILICATE" SYSTEMS

As long as the monovalent ions, such as the Cl and NO_3 anions and the alkali cations, are the only diffusible ions present in the system, flocculation is confined to a narrow zone on either side of the isoelectric point. We have

already studied the effect of the presence of a divalent anion, i.e., the SO_4 ion. The effect was twofold: The flocculating zone was greatly extended on the positive side of the isoelectric point; and the composition ratio of silica to sesquioxides in the isoelectric complex was markedly reduced (compare tables 40a and 40b).

The divalent cations have already been shown (9) to have the opposite effect to that of the SO_4 ion. In the presence of divalent cations the composition ratio of the isoelectric complex may exceed the ratio of 3. This does not mean that more than 3 mols of silica are in actual combination with one mol of sesquioxide. It is evident that some of the silicate valences are linked with the divalent cations, which accounts for the high ratio. There is evidently also no limit to the amount of excess silica which may thus be fixed in the complex, but once the silica content exceeds a certain proportion, the complex ceases to be amphoteric; it remains negative at all pH values.

The presence of divalent cations also extends the zone of flocculation on the negative side of the isoelectric point. No matter how strongly negative the sol may be it will flocculate at once if sufficient $Ca(OH)_2$ is added. The silica will then all be carried down in the floc and if the ratio of silica to sesquioxide in the mixture is high the composition ratio in the floc will be equally high and the complex will be strictly electronegative.

If a high proporton of silica be isoelectrically precipitated as in the concentrated systems in tables 42a and 42b, and if, after mixing, the system be diluted and the pH be adjusted to that of the isoelectric value of the dilute systems in tables 41a and 41b, it is found that the composition ratio is intermediate between that of the concentrated and the dilute systems. In other words, the silica, being of a colloidal nature, is not completely reversible. If any isoelectric silicate gel is dried the reversibility is greatly reduced. This will explain the great stability of the natural soil colloids which may have been subjected to alternate drying and wetting and, more important, to the process of aging which leads to a coarser structure and evidently also to a certain degree of crystallization, as shown by X-ray photographs (3).

INFLUENCE OF THE $\frac{SiO_2}{R_2O_3}$ RATIO ON THE ADSORPTIVE AND ELECTROKINETIC BEHAVIOR OF THE NATURAL SOIL COLLOIDS

Two tables which have appeared in a previous publication (8) are given here in a condensed form. Table 45 shows the adsorption of the PO_4, SO_4, and Cl ions from solutions of the respective acids by a series of soil colloids of varying silica/sesquioxide ratio. The charge and speed of electrical migration are also shown. Table 46 shows the adsorption of the same ions from a mixture of the acid with increasing proportions of ammonia, by the Norfolk soil colloid.

For a detailed discussion of these experiments the reader is referred to the

original paper. For our present subject the following points of comparison are of interest:

The anion adsorption increases with a decrease in the silica/sesquioxide ratio. The increase in adsorption is greater than the absolute increase in the sesquioxides per gram colloid. This indicates that the silica and sesquioxides exist in a more or less stable combination. Colloids very high in silica, like the Bentonie and Fallon, do not adsorb any

TABLE 45

Adsorption of the PO_4, SO_4, and Cl ions from solutions of the respective acids by different soil colloids

Initial concentrations: H_3PO_4, 1.768; H_2SO_4, 1.624; HCl, 1.640; milliequivalent in 100 cc.

COLLOID 1 GM.	$\frac{SiO_2}{R_2O_3}$	PO_4		SO_4		Cl	
		Adsorbed milliequivalent per gram	μ/sec. 1 volt/cm.	Adsorbed milliequivalent per gram	μ/sec. 1 volt/cm.	Adsorbed milliequivalent per gram	μ/sec. 1 volt/cm.
Bentonite	3.81	0.214	−2.3	−0.005	N.D.	N.D.	N.D.
Fallon	3.82	0.518	−1.0	−0.003	−1.1	−0.004	−0.6
Sharkey	3.18	0.700	−1.3	0.036	−0.8	0.004	−0.4
Marshall	2.82	0.932	−0.7	0.041	−0.7	Lost	−0.2
Sassafras	1.89	1.152	+0.2	0.151	−0.2	0.034	+1.4
Norfolk	1.63	0.904	+0.6	0.129	−0.1	0.026	+1.7
Aragon	0.55	1.601	+1.3	0.269	+0.6	0.044	+2.8

TABLE 46

Adsorption of the PO_4, SO_4, and Cl ions from solutions of the respective acids, with various additions of ammonia, by the Norfolk soil colloid

Initial concentrations: H_3PO_4, 6.14; H_2SO_4, 5.41; HCl, 5.05; milliequivalent in 50 cc.

NH_3 ADDED MILLIEQUIVALENT IN 50 CC.	PO_4			SO_4			Cl		
	Adsorbed milliequivalent per gram	pH	μ/sec. 1 volt/cm.	Adsorbed milliequivalent per gram	pH	μ/sec. 1 volt/cm.	Adsorbed milliequivalent per gram	pH	μ/sec. 1 volt/cm.
0.0	0.84		+1.1	0.164		−0.5	0.079		N.D.
1.287	0.88	<4.4	−0.9	0.163		−0.9	0.075		+1.7
2.574	0.56	6.2	−3.5	0.121		−1.2	0.060		+1.4
3.861	0.42	6.8	−3.6	0.096		−1.4	0.037		+1.1
5.148	Lost	>8.0	−3.8	0.071	<4.4	−1.5	0.017	<4.4	+0.1
7.722	0.27		−4.1	−0.031	>8.0	−3.6	−0.019	>8.0	−3.3

sulfuric or hydrochloric acid. (Where there is no positive adsorption a negative adsorption due to the Donnan distribution is observed.) All of the sesquioxides are apparently here in combination with the silica.

The PO_4 is much more strongly adsorbed than the SO_4 ion and the SO_4 more strongly than the Cl ion. The relative order of magnitudes is not very different from that observed in the isoelectric precipitates. The Bentonite and the Fallon colloids, which adsorb neither SO_4 nor Cl ions, adsorb considerable quantities of the PO_4 ion. Whether this is due to a

displacement of silica or to the formation of an addition compound, or both, will be discussed in a later section.

The quantities of the various ions adsorbed decrease with an increase in pH, the PO_4 ion being the only ion which is adsorbed from an alkaline solution.

Soil colloids having a low silica/sesquioxide ratio and adsorbing the greatest quantities of anions become electropositive in acid solutions. The isoelectric point lies at a higher pH the higher the sesquioxide content. The relationship is therefore the same as that found to govern the isoelectric precipitates. The divalent SO_4 ion is not as highly dissociated by the complex as the monovalent Cl and H_2PO_4 ions. (At low pH values the phosphate ion is chiefly monovalent). The positive charge therefore attains higher values in the H_3PO_4 and HCl solutions than in that of the H_2SO_4. The same phenomenom was met with in the foregoing synthetic sols.

FACTORS GOVERNING THE COMPOSITION OF THE INORGANIC SOIL COLLOIDS

The lithosphere has, according to Clarke (1), the following average composition: SiO_2, 59.85; Al_2O_3 + Fe_2O_3, 21.35; CaO, 4.81; MgO, 3.77; K_2O, 3.02; and Na_2O, 3.29 per cent. If the Fe_2O_3 is assumed to constitute one-fourth of the total sesquioxides, a silica/sesquioxide ratio equal to 5.2 is reached. This is higher even than that of the highest soil colloid ratios but since some of the silica (about 12 per cent) exists in the form of highly insoluble quartz we cannot expect such a high ratio in the colloids.

When rocks weather under arid conditions, there is little or no loss of material. Most of the products of hydrolysis remain in the soil and react with one another to form a colloidal complex, doubtless in accordance with the same laws we have found to govern the formation of the complexes described in the foregoing chapters. The sesquioxides will combine with a certain proportion of the silica and, in the presence of an abundance of divalent bases, the remainder of the silica will be precipitated by them. The complex will therefore have a high silica/sesquioxide ratio and be a strictly electronegative complex. It will owe its stability to the presence of the divalent cations. Soil colloids high in silica and bases occur chiefly in arid regions, as shown by the very valuable work of Robinson and Holmes (16).

Suppose, for the sake of continuity in our line of reasoning, that the aridity is changed into great humidity. Under such conditions, what would happen to the colloidal soil complex would indirectly depend upon another dominating factor, namely, the temperature. Whether in the tropics or in the cold regions, the soil would be subjected to great leaching, and the bases, and with them the protected silica, would be progressively washed out. In the colder regions there would be an accumulation of organic matter and the consequent development of a high soil acidity, but this would not happen in tropical regions. In the tropics there is no accumulation of humus. This, together with more intense weathering, keeps up a small but constant supply of bases, and maintains, in spite of the leaching, a more nearly neutral reaction.

The acid reaction on the one side and the more nearly neutral reaction on the other would have a profound influence upon the composition of the colloidal complex, if we can draw any inference from the foregoing study.

It has been shown that in the absence of divalent bases the sesquioxides precipitate with silica a complex which is richer in sesquioxides and poorer in silica, the higher the pH. We should evidently, therefore, expect to find the soil colloids in the humid, tropical regions possessing a low silica/sesquioxide ratio whereas the soil colloids in the temperate and cold, humid regions, where the soil reaction is more acid (evidently in the absence of carbonates), would be expected to possess a higher silica/sesquioxide ratio. Thus we know that the laterites which contain very little silica are the result of tropical, humid weathering. The work of Robinson and Holmes (16) seems to bear out the second point.

The silica/sesquioxide complex is both chemically and electrokinetically an amphoteric complex. It combines with acids and becomes thereby electropositive because in this condition it dissociates diffusible anions. It combines with bases and becomes thereby electronegative because in this condition it dissociates, diffusible cations. It follows that, if by leaching, dialysis, or otherwise, the diffusible ions be removed, the complex will approach or attain the isoelectric condition. This condition represents, therefore, the ultimate and the most stable condition. It has been pointed out that colloids are most easily "purified" at the isoelectric point. Conversely if an amphoteric colloid be "purified" it will be brought nearer its isoelectric point. Since the silica/sesquioxide ratio in the isoelectric aluminum and ferric "silicates" is higher the lower the pH, and vice versa, we arrive at the very important deduction that the most stable, and therefore the ultimate, composition of the soil complex will depend upon the pH of the leaching soil solution. The more acid the soil solution the greater will be the proportion of silica remaining precipitated with the sesquioxides after the bases and a portion of the silica have been removed by leaching.

It has been noted by Zakharov (21) that desilication is more rapid and extensive in the humid, tropical regions than in the humid, temperate regions, resulting in the former in the formation of laterites and in the latter in the formation of clays. The presence of the earth carbonates will, under all conditions, delay the desilication because these substances will maintain a saturated and stable condition of the negative complex.

An attempt was made in the foregoing section (11) to represent the size of the colloidal particle as an equilibrium condition between two sets of opposing forces. The higher the exchange capacity and the higher, therefore, the micellar ion density, the greater, it was concluded, must be the degree of dispersion. Since the exchange capacity decreases with the silica/sesquioxide ratio we should expect a lower dispersion, i.e., a larger particle size, and a less plastic and an, all around, less colloidal condition of the complex, the greater the degree of desilication. This is also the case, for the laterites are known to be non-plastic and very difficult to disperse. They also have a tendency to form non-dispersible concretions. This is not surprising when it is considered that their silica content is often so low that their isoelectric point lies

well within the prevailing range of pH values. At the isoelectric point the particles have no ion atmosphere and carry therefore no charge and no water of osmotic hydration. Stripped of the forces by virtue of which the particles can exist as independent micellae, there is nothing to prevent them from cohering into larger and larger units.

Whereas the formation of laterite, and also bauxite, must be the result of the removal of bases and silica from the soil complex under approximately neutral conditions, the formation of kaolinite must result from the same process under acid conditions. For one mol of the Al_2O_3 to retain two mols of SiO_2 after the removal of all cations would require a fairly high acidity. At the high degree of dilution of the soil solution the pH would doubtless have to be below 5. Kaolinite is itself isoelectric between the pH values of 4 and 5 (9). Kaolinite, which is coarsely crystalline as compared to soil colloids and which contains practically no bases, may be assumed to be formed when a colloidal complex of the composition $Al_2O_3 \cdot 2\ SiO_2$ is subjected for a great length of time to a hydrogen-ion concentration at or near that of the isoelectric pH of the complex. That kaolinite formation is connected with an acid medium is brought out by the work of Wüst (20), who ascribes it to the action of humus, and by Rösler (19), who assumes it to be a result of pneumatolytic action, i.e., acid gases.

Hydrous aluminum silicates containing a higher proportion of silica, such a beidellite and scolecite with a silica/sesquioxide ratio *about* 3 and pyrophyllite and Montmorillonite with a ratio from *about* 4 to 5 (18), contain always a certain proportion of bases which usually increases with the proportion of silica. These materials have not been desilicated, that is, they have not been degraded by leaching to any great extent, as is indicated by the presence of readily exchangeable cations. It is evidently because of the presence of bases, especially of the divalent cations, that a complex with such high proportions of silica could precipitate out in the first place. Left more or less unaltered for a long time, crystallization has progressed more or less extensively, giving rise to compounds of definite composition and to a greater stability. Some of the bases are locked up within the crystals and become non-exchangeable. (Only about one-third of the bases present in the natural materials are readily exchangeable.)

THE LAW OF DEFINITE PROPORTIONS

The definiteness in composition reported for these hydrous silicates, even when "purified," should not be uncritically accepted. Their composition is as indefinite as their nomenclature. Within the crystal lattice the law of definite proportions doubtless holds. On the surface (and the surface is great in highly dispersed materials) there is no such definiteness. Every ion in the dispersion medium enters into a very complicated exchange equilibrium. The hydroxyl, the phosphate, the "humate," the sulfate, and a number of other anions may displace the silicate ion. Iron displaces aluminum and

vice versa. Every cation in the solution displaces any cation in the complex according to the activity of each. The more highly dispersed the crystalline material is, the more indefinite its composition. Then, crystallization is often very incomplete. Highly insoluble materials, like most colloids, are slow to crystallize and can do so only to the extent that ions which will fit into the crystal lattice are available. It is obvious that a highly heterogenous complex cannot crystallize. When crystallization does take place there must be a change in the composition. The proper ions are selected and the ions which do not fit are rejected. Some of the "adsorbed" ions pass into solution. This explains the reversion of adsorption as a result of aging as first observed by Freundlich and Hase (2).

CHARGE AND CRYSTALLIZATION

The highly silicated, electronegative soil colloids which contain a high proportion of displaceable cations are very fine-grained. Yet it has been shown that they are at least partly crystalline. Since the solubility decreases with an increase in crystal size by virtue of a decreased curvature we might wonder why it is that the crystalline material in soil colloids attains only submicroscopic dimensions. This may be due to the heterogenous makeup of the adsorption layer. It has been shown by Marc (7) that adsorbed ions of a different kind retard crystallization, but it seems probable that the charge resulting from dissociation limits the dimensions of the crystals just as it places a limit on aggregation; crystallization being in effect nothing but an orderly aggregation of ions. Crystallization might also be looked upon as an adsorption of ions which together fit into the symmetrical arrangement characteristic of the crystal lattice. If crystallization is to proceed, the rate of adsorption of the two ions must be equal. If one ion is very large, and, because of a low self-potential, is incapable of an independent existence, while the other ion has a great solution stability and remains dissociated, a noncrystalline, highly charged micelle (as in a soap solution) will result. If the two ions enter the lattice with about equal energy, the charge will be small and the crystallization can proceed unimpeded. If the two ions enter with different energy, one of the ions remaining dissociated in considerable excess, the charge will be high and the most adsorbable ion will be entering the lattice against a steep potential gradient. Why a crystal may form under such conditions and yet remain very small in size as in the case of soil colloids is brought out by the following.

Assuming a potential difference $\zeta = 70$ millivolts, a thickness of the double layer $\delta = 5\mu\mu$ and a dielectric constant $D = 81$, von Hevesy (4) calculates the charge e for particles of different radii from the formula:

$$e = \frac{\zeta D r (r + \delta)}{\delta}$$

and obtains the figures shown in the first and second columns in table 47. By dividing the number of electronic charges on each particle by the square of the radius we get the values in the third column, which represent the relative number of charges per unit surface, or the ionic density on the different size particles.

If crystallization cannot proceed against a potential gradient above a certain maximum we might easily explain why a crystal will form and grow to a certain small size and then no more. On very small particles the ionic density required for the usual maximum potential of 70 millivolts is very great, greater probably than the dissociation. The smallest crystal rudiments would therefore, like very large ions, have a low potential. The crystal would grow until the potential attained the critical value. Needle-shaped and micaseous crystals having points of high curvature might, however, grow indefinitely. Concave areas could not grow, because here the potential would reach a maximum at very slight dissociation. As the dissociation is probably different on different crystal faces the growth would vary accordingly. In concen-

TABLE 47

Number of ions and ion density necessary to charge particles of different size to the same potential

r	CHARGE OF PARTICLE IN NUMBER OF ELECTRONS	CHARGES PER UNIT SURFACE OR RELATIVE ION DENSITY
$\mu\mu$		
1	6	6.00
2	14	3.50
10	120	1.20
24	550	0.95
100	8,550	0.85
240	47,000	0.82

trated solutions crystals may grow to large dimensions because here the potential is annihilated by the high ion concentration. Very soluble salts accordingly form large crystals.

The quantitative relationship in table 47 may be qualitatively demonstrated, as in figure 7. It is obvious that to produce the same density in the ion atmosphere a greater number of ions must dissociate per unit surface (a) the greater the curvature, i.e., the smaller the particle, since the dissociated ions must then diffuse into a conical expansion of space which becomes greater as the radius of the particles becomes smaller. It should be pointed out that if a greater average thickness δ of the double layer is assumed, which would be justified on the basis of the r_1/r ratios in table 12 (part I), the difference in ion density necessary to give the same potential for large and for very small particles would become very much greater than the difference shown in table 47.

If the degree of dissociation is limited, then the ion density over a very curved surface may never attain the value it will over a less curved surface, i.e., around a larger particle. Assuming this to be the case it can be shown

that the dissolved (free) ions in the solution will be in higher concentration within the less dense micellar ion atmosphere over a highly convex surface than in the more dense ion atmosphere over a less convex surface. This follows from the Donnan equilibrium equation (see part I) which, for a uni-univalent compound, is

$$x_2 = y(y + z)$$

Where the value of z (i.e., the micellar ion concentration) is small, y (the free ion concentration within the atmosphere) will obviously not be so much smaller

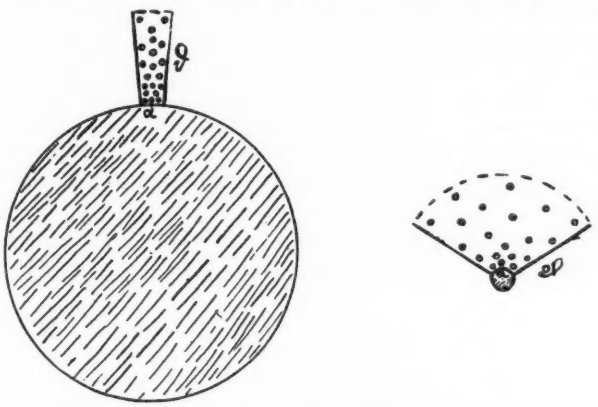


FIG. 7. THE RELATION BETWEEN PARTICLE SIZE OR CURVATURE AND THE ION DENSITY IN THE MICELLAR ATMOSPHERE AT THE SAME DEGREE OF DISSOCIATION PER UNIT SURFACE

than x (the outside ion concentration) as where the value of z is larger. This means further that the Donnan potential

$$\text{P.D.} = \frac{58}{2} \log \left(1 + \frac{z}{y}\right)$$

will be lower between the less dense ion atmosphere and the outside solution than between this solution and the more dense ion atmosphere over a less convex or plane surface. Both of these factors would favor a more rapid deposition of the ions in the solution on surfaces of very great convexity. The higher the valence of the ion with the same sign of charge as that of the interface the greater would be this effect.

If the degree of dissociation is limited then very small particles should show a slower cataphoresis than the larger. This has never been proved and probably never will even if the assumption is correct, because such particles can only have a transient existence, for being unstable they must grow to larger dimensions. To what extent the electrokinetic potential influences the growth of

crystals must be left undecided, the author has merely suggested the possibility of such an influence.

SUMMARY

Isoelectric precipitates of aluminum and ferric "hydroxides" were prepared from the respective chlorides and sulfates. The sulfated hydroxides are isoelectric at a lower pH than the chloridated complex. The SO_4 content of the former is higher than the Cl content in the latter. The ferric complex is isoelectric at a lower pH than the aluminum complex.

The entrance of the phosphate and silicate ions into the sesquioxide complex lowers the isoelectric pH because these ions displace the diffusible acid anions as well as the hydroxyl ions. There are many isoelectric "phosphates" and "silicates." The more highly phosphated or silicated the complex the lower is the isoelectric pH. The lower the phosphate or silicate concentrations in the solution the greater is the relative proportion entering into combination. In high concentrations of the phosphate and silicate ions the isoelectric complex approaches but never attains full saturation, i.e., $P_2O_5/Al_2O_3 = 1$ and $SiO_2/Al_2O_3 = 3$, provided that other cations which form insoluble phosphates and silicates are absent, and that colloidal silica is not precipitated with the complex.

All the ions in the system mutually displace one another according to the energy of each. At the isoelectric point there is always a certain small number of diffusible anions in combination. At that point the anionic and cationic dissociation must be equal. There is a balance between cations and anions in the complex, but a stoichiometrical relationship between any two ions must be accidental and should not be looked for even when the colloid is "purified." This applies to the more or less crystalline natural colloids as well, for although the law of definite proportions must hold as far as the interior of the crystal is concerned, there is no such definiteness on the surface, which is very great in the colloids. The adsorption layer is very complex in its make-up and changes constantly with the conditions, such as the nature and concentrations of the ions in the solution, the pH, and the temperature.

The work herein described will serve to explain the occurrence of the highly silicated and base-saturated soil colloids in the arid regions, the moderately silicated and more or less base-unsaturated soil colloids in the temperate and colder humid regions, and the almost completely desilicated and base-unsaturated soil colloids in the humid tropical regions.

Another paper (part IV) dealing with the isoelectric aluminum and ferric "humates" is now being prepared.

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AUTHOR INDEX

Barnette, R. M., and Hester, J. B. Influence of inorganic nitrogen compounds on reaction and replaceable bases of Norfolk sand, 431–437.

Bodman, G. B., and Tamachi, M. Studies of soils in the plastic state, 175–195.

Bouyoucos, George John. The indirect determination of various soil characteristics by the hydrometer method, 267–272.

Bradley, Leon A., and Fuller, James E. Nitrogen fixation in field soil under different conditions of cropping and soil treatment, 49–57.

Brown, P. E. *See* **Walker, R. H.**

Burke, Victor, amd Hohl, Nelson J. Cross inoculation with Rhizobium radicicolum, 407–411.

Chapman, H. D., and Kelley, W. P. The determination of the replaceable bases and the base-exchange capacity of soils, 391–406.

Clark, F. M. *See* **Sears, O. H.**

Cooper, H. P., and Wilson, J. K. Relation of ash constituents of pasture plants to the oxidation-reduction potentials of nutrients, 421–430.

Das, Surendralal. An improved method for the determination of available phosphoric acid of soils, 33–48.

Dean, A. L. Nitrogen and organic matter in Hawaiian pineapple soils, 439–442.

Doolas, George Z. Local variation of soil acidity in relation to soybean inoculation, 273–287.

Dreibelbis, F. R. *See* **Schollenberger, C. J.**

Fuller, James E. *See* **Lyon, T. L.**

Gainey, P. L. *See* **Sewell, M. C.**

Hester, J. B. *See* **Barnette, R. M.**

Hohl, Nelson J. *See* **Burke, Victor.**

Humfeld, Harry. A method for measuring carbon dioxide evolution from soil, 1–11.

Jensen, H. L. Actinomycetes in Danish soils, 59–77.

Kelley, W. P. *See* **Chapman, H. D.**

Leighty, Wilbur R., and Shorey, Edmund C. Some carbon-nitrogen relations in soils 257–266.

Leonard, Lewis T., and Reed, H. R. A comparison of some nodule forming and non-nodule forming legumes for green manuring, 231–236.

MacIntire, W. H., Shaw, W. M., and Young, J. B. The oxidation of pyrite and sulfur as influenced by lime and magnesia—a 12-year lysimeter study, 443–457.

Magistad, O. C. Rate of loss of replaceable potassium by leaching, 243–256.

Mann, H. B. Availability of manganese and of iron as affected by application of calcium and magnesium carbonates to the soil, 117–141.

Mattson, Sante. The laws of soil colloidal behavior: III. Isoelectric precipitates, 459–495.

Phillips, Max, Weihe, Herman D., and Smith, N. R. The decomposition of lignified materials by soil microörganisms, 383–390.

Puri, Amar Hath. Electrofiltration: a new method of removing exchangeable bases from soil colloids, 413–419.

Ravikovitch, S. Lime requirements in differently fertilized soils, 79–95.

Reed, H. R. *See* **Leonard, Lewis T.**

Robinson, W. O. Some chemical phases of submerged soil conditions, 197–217.

Schollenberger, C. J. Determination of carbonates in soil, 307–324.

Schollenberger, C. J., and Dreibelbis, F. R. Analytical methods in base exchange investigations on soils, 161–173.

Sears, O. H. Relation of nitrates in soils to the response of crops to potash fertilization: I. Factors contributing to the unproductiveness of "alkali" soils in Illinois, 325–347.

Sears, O. H., and Clark, F. M. Nonreciprocal cross-inoculation of legume nodule bacteria, 237–242.

Sewell, M. C., and Gainey, P. L. Interrelation of nutrients and soil reaction on growth and inoculation of alfalfa, 297–305.

Shaw, W. M. *See* **MacIntire, W. H.,** and Young, J. B.

Shorey, Edmund C. *See* **Leighty, Wilbur R.**

Smith, N. R. *See* **Phillips, Max,** Weihe, Herman, and.

Stevens, Kenneth R. *See* **Waksman, Selman A.**

Tamachi, M. *See* **Bodman, G. B.**

Tenney, Florence G., and Waksman, Selman A. Composition of natural organic materials and their decomposition in the soil: V. Decomposition of various chemical constituents in plant materials, under anaerobic conditions, 143–160.

Tidmore, J. W. Phosphate studies in solution cultures, 13–31.

Turner, P. E. The state of unsaturation of the soil in relation to its field behavior and lime requirement, 349–381.

Waksman, Selman A. *See* **Tenney, Florence G.**

Waksman, Selman A., and Stevens, Kenneth R. A critical study for determining the nature and abundance of soil organic matter, 97–116.

Walker, R. H., and Brown, P. E. Some fermentation characteristics of various strains of Rhizobium meliloti and Rhizobium japonicum, 219–229.

Weihe, Herman D. *See* **Phillips, Max,** and Smith, N. R.

Wilson, J. K. Seasonal variation in the number of two species of Rhizobium in soil, 289–296; *See* **Cooper, H. P.**

Young, J. B. *See* **MacIntire, W. H.,** and.

SUBJECT INDEX

Acidity, actinomycetes resistance to, 73.
Actinomycetes—
  description of various groups, 64.
  in Danish soils, 59–77.
  physiological studies with various, 68.
Aerobic decomposition of plants, 143–160.
Alfalfa—
  aerobic decomposition of, 158.
  anaerobic decomposition of, 158.
  decomposition of, plants, 151.
  inoculation and growth of, as influenced by reaction and nutrients of soil, 297–305.
Alkali—
  exchangeable, acetate method, 169.
  soils—
    composition of three, 338.
    unproductiveness of, factors contributing to, 325.
Aluminum—
  extraction of, with ammonium acetate, 170.
  hydroxide, isoelectric, 460.
  phosphate, isoelectric, 467.
Ammonium—
  absorbed, determination of, 171.
  acetate as a base exchange salt, 161.
  exchangeable, determination of, 171.
  sulfate, effect on replaceable bases, 434.
Anaerobic decomposition of plants, 143–160.
Anion adsorption of soil colloids, 487.
Bacteria—
  number of, in field soils various fertilized, 52.
  radicicola, viability in acid soils, 281.
  Rhizobium—
    meliloti and japonicum, fermentation characteristics of, 219–229.
    radicicolum, cross inoculation with, 407–411.
    seasonal variations in number of, 289–296.
Base exchange—
  ammonia absorption method, 398.
  capacity of soils, determination of, 391–406.
  carbonates dissolved with ammonium acetate as, salt, 172.
  methods of investigation, 161–173, 398, 413.
Bases—
  exchangeable—
    estimation of, 416.
    in limed soils, 84.
    in unlimed soils, 84.
    method of removing, from soil colloids, 413–419.
  replaceable—
    in soils, determination of, 392.
    nitrogen inorganic, influence of, on, 431.
Calcium—
  carbonate—
    reserve needed in soils, 374.
    solubility of, in NaCl, 82.
  carbonate, effect on—
    actinomycetes in acid soils, 62.
    exchangeable calcium, 85.
    hydrogen-ion concentration of some soils, 123.
    manganese and iron availability in soil, 117.
  exchangeable, 364.
  exchangeable, as affected by—
    errors due to sampling, 353.
    fertilizer treatment, 86.
  exchangeable methods—
    acetate, 168.
    different, 394.
    Gedroiz, 82.
    Hissink, 82, 368, 394.
    Tyurin, 82.
Carbohydrates, organic acid formation from, by actinomycetes, 70.
Carbon—
  dioxide—
    apparatus used in measuring, 2.
    effect on solubility of submerged soil constituents, 205.
    method of measuring, 1–11.
    review of methods, 308.
  nitrogen ratio relations, 257–266.

Carbonates, determination of, in soil, 307.
Cations—*see* also Bases, Base exchange.
exchangeable in soils, 79–95.
Colloid—
clay content determination, 190.
determination of, content of soils indirectly, 270.
Colloidal—
complex of soil, absorption of nutrient ions, 425.
laws of soil, behavior, 459–495.
Colloids—
anion adsorption by, 487.
removing exchangeable bases from soil, 413–419.
soil, factors governing the composition of inorganic, 488.
soil, influence of $\frac{SiO_2}{R_2O_3}$ ratio on, 486.
Corn—
aerobic decomposition of, 157.
anaerobic decomposition of, 157.
carbon dioxide evolution from soil in, 6.
phosphate content of, sap, 26.
potash experiments with, 329.
stalks, composition of, 146.
titration curves for sap from, 26.
Crop rotation experiments, 49.
Culture solution, *see* Nutrient solution.
Definite proportions, law of, 490.
Diastase formation by actinomycetes, 71.
Dilatometer method modification, 267.
Electric charge and crystallization, 491.
Electrofiltration as a method of removing bases, 413–419.
Fertilizer—*see* also Nitrogen, Potassium, Phosphate, Phosphorus.
effect on—
exchangeable calcium, 86.
soybean growth and composition, 128.
experiments in Massachusetts, 50.
potash—
absorption of, salts, 339.
response of crops to, 325–347.
Hydrogen—
exchangeable, Mattson method of determining, 83.
peroxide extraction of soils, 190.
replacement of, in soils, 400.
Hydrogen-ion concentration—
effect on—
lime requirement, 92.
nitrogen fixation, 56.
phosphate absorption, 28.
in various media for actinomycetes, 70–74.
Hydrometer method for determining soil characteristics, 267.
Invertase formation by actinomycetes, 71.
Ion density, relation between particle size of curvature and, 493.
Iron—
availability of, in soil, 117.
hydroxide, isoelectric, 460.
in bog water, 198.
phosphate, isoelectric, 467.
solubility of—
as influenced by time of extraction, 199.
in various soils, 119.
Isoelectric precipitates, 459.
Legumes, nodule forming and non-nodule, for green manuring, 231–242.
Lettuce, potash experiments on, 327.
Lignin, decomposition of, by soil microorganisms, 383.
Lime—
effect on—
exchangeable calcium, 85.
physical condition of soil, 358.
pyrite oxidation, 443.
sulfur oxidation, 443.
requirement, determination on basis of degree of unsaturation, 370.
requirement, relation to—
exchangeable cations, 79–95.
hydrogen-ion concentration, 92.
unsaturation of soil, 349–381.
snail shells as, their composition, 337.
Lysimeters, a 12-year study, 443.
Magnesium—
carbonate, effect on—
hydrogen-ion concentration of soil, 123.
manganese and iron availability in soil, 117.
pyrite oxidation, 443.
sulfur oxidation, 443.
exchangeable—
acetate method, 168.
Manganese—
availability of, in soil, 117.
determination of, in various soils, 119.
in bog water, 198.
solubility of, as affected by—
carbon dioxide, 205.
time of extraction, 199.
solubility of, in various soils, 119.

Micellar atmosphere, relation between particle size or curvature and the ion density in the, 493.
Microörganisms, lignified materials, decomposition of, by soil, 383–390.
Moisture equivalent, determination of, 188, 269.
Nitrate accumulation of, as influenced by moisture, 333.
Nitrates—
  potash fertilization and, in soils, 325.
Nutrient—
  media for—
    actinomycetes, 70.
  solution—
    corn in, 15.
    phosphate studies, 13–31.
    sorghum in, 15.
    tomatoes in, 15.
Nitrite formation by actinomycetes, 70.
Nitrogen—
  fixation, as affected by—
    cropping, 49–57.
    soil treatment, 49–57.
  in Hawaiian soils, 439.
  inorganic, influence of, on reaction and bases of Norfolk sand, 431–437.
  losses from alfalfa decomposition, 153.
Oak leaves, composition of, 150.
Organic matter—
  anaerobic decomposition of, 143.
  chlorine dioxide extraction of, 100.
  hydrogen-peroxide extraction of, 100.
  in Hawaiian soils, 439–442.
  methods for determining, 97–116.
  natural, composition and decomposition of, 143–160.
Oxidation-reduction potentials of nutrients, relation to ash constituents of pasture plants, 421–430.
Phosphate—
  absorption of, by plants of various pH, 28.
  concentration and pH, relation to composition of isoelectric precipitates of Al and Fe phosphates, 468.
  maximae for tomatoes, corn, and sorghum, 31.
  solution cultures, studies in, 13–31.
Phosphoric acid—*see* also Soils phosphoric acid.
  citric acid versus K_2CO_3 method for determining available, 36–42.
  method of determining available, in soils, 33–48.
Plant—
  chlorosis treatment, 129.
  growth, rate of, 20.
  materials, decomposition of, under anaerobic conditions, 143–160.
  sap—
    buffer capacity of, 25.
    phosphate content of, 17, 23.
Plants—
  analysis of pasture, 422, 424.
  ash constituents of pasture, relation to oxidation-reduction potentials of nutrients, 421–430.
  chlorosis of, as corrected by foliage treatment, 129.
  light requirements of, relation to their food value and soil fertility, 427.
  wilting coefficient of, determination by hydrometer method, 270.
Plasticity of soils, 180.
Potassium—
  carbonate method for determining available phosphorus, 48.
  replaceable, rate of loss by leaching, 243–256.
  soil, availability of, 338.
Proteolytic activity of actinomycetes, 72.
Pyrite, oxidation of, as influenced by lime and magnesia, 443–457.
Silica sesquioxide ratio influence on adsorptive behavior and electrokinetic behavior of soil colloids, 486.
Silicate, sulfated complex, 476.
Silicates—
  effect of divalent cations on, 485.
  iron and aluminum, isoelectric precipitates, 468, 472.
  isoelectric, effect of dilution on the pH and composition of, 479.
Snail shells, composition of, 337.
Soil—
  acidity, relation to soybean inoculation, 273–287.
  bacteria, *see* Bacteria.
  carbon dioxide evolution from, 1–11.
  carbonates—
    apparatus for the determination of, 315.
    determination of, 307–324.
  characteristics, determination by hydrometer method, 267–272.

colloids—
determination by indirect methods, 270.
total, 269.
colloids, *see* colloid, colloids.
fallow, carbon dioxide evolution in, 6.
fertility, relation to light requirements of plants, 427.
iron availability in, 117–141.
manganese availability in, 117–141.
microörganisms, *see* Microörganisms.
nitrogen, fixation of, in field, 49–57.
organic matter, *see* Organic matter.
reaction—*see* also H-ion concentration, Soil acidity.
influence of inorganic nitrogen on, 431.
saturation capacity, errors in determining, 353, 355, 363.
solution—
composition of submerged, 203.
displaced, composition of, 341.
plant growth in, 30.
submerged, reaction of, 206.
submerged—
chemical phases of, 197–217.
gases from, 208.
toxicity of, 212.
unsaturation, relation to lime requirement, 349–381.
Soils—
acid—
actinomycetes in, 62.
available phosphoric acid in, 37.
alkali—*see* also Alkali.
available phosphoric acid in, 40.
base exchange in, *see* Base exchange.
British West Indies, description of some, 361.
carbon-nitrogen relations in, 257–266.
chlorosis of soybeans on limed, 128.
Danish, actinomycetes in, 59–77.
exchangeable cations and lime requirement in, 79–95.
forest, actinomycetes in, 61.
Hawaiian, nitrogen and organic matter in, 439–442.
heath, actinomycetes, in, 61.
humus, available phosphoric acid in, 37.
hydrogen peroxide digestion of, 190.
laterite, available phosphoric acid in, 38.
marsh, actinomycetes in, 61.
mechanical analysis of, by electrofiltration, 417.
moor, actinomycetes in, 61.
nitrates in, relation to the response of crops to potash fertilization, 325–347.
phosphoric acid—
methods of determining available, 33–48.
total and available in, 44.
plastic state of, 175–195.
unsaturation of, 88.
Solution cultures, phosphate studies in, 13–31. *See* also Nutrient solutions.
Sorghum—
phosphate content of, 27.
titration curve of, stems, 27.
Soybeans—
as affected by—
calcium carbonate, 124.
fertilization, 128.
hydrogen-ion concentration, 277–281.
magnesium carbonate, 124.
carbon-dioxide evolution from soil under, 6.
chlorosis of, on limed soils, 128.
Sphagnum plants, composition of, 154.
Straw—
composition of rye, 148.
use of, for alkali soils, 330.
Sulfated, silicate complex, 476.
Sulfur, oxidation of, as influenced by lime and magnesia, 443–457.
Tomato—
phosphate content of, 27.
titration curve of, stems, 27.
Wheat, potash experiments on, 327.
Water—
unfree, determination of, in soils, 269.
vapor absorption by soils, 190.
colloid-clay content by the method of, 190.
Wilting coefficient, determination of by hydrometer, 270.

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